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Phase Transition During Heat Treatment in TiO_2 Films Prepared by Atomic Layer Deposition

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The process of obtaining a thin TiO_2 film on a silicon substrate using atomic layer deposition is described. The study investigates the phase transition in these films from the anatase to rutile polymorphs under various heat treatment conditions. Raman spectroscopy, X-ray diffraction, and atomic force microscopy are used to analyze the structural changes and surface morphology of the films before and after thermal treatment. Analytical data confirm that the anatase TiO_2 polymorph grows during thermal atomic layer deposition using titanium tetra-isopropoxide and water as precursors, resulting in a polycrystalline film. During thermal treatment, a complete transition from anatase to rutile for a $1.5\,\mu$m thick film on a silicon substrate occurs after 2 to 3 hours at 1000°C.

Keywords: titanium dioxide film, anatase, rutile, atomic layer deposition, phase transition, Raman spectroscopy, atomic force microscopy.

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1. Introduction

There are several polymorphous forms of titanium dioxide (TiO_2): stable rutile phase, as well as metastable anatase and brookite [1,2]. Rutile and anatase have a tetragonal crystalline structure with various dimensional groups [3–5]. All phases TiO_2 may manifest different electrical and structural properties due to the difference in the crystalline structure [2,6,7]. Samples TiO_2 with different crystalline structure may be applied in various fields. For example, in medicine [8,9], photocatalysis [10,11], photo-electrics [1,12], as well as in micro- and nanoelectronics [13,14].

There are several ways of fabricating TiO_2 thin films, including sol-gel method [15], reactive magnetron sputtering [2], solvothermal synthesis [6], thermal oxidation [16], atomic layer deposition (ALD) [7] and others. Depending on conditions of synthesis and selected method, the obtained samples TiO_2 may have a different morphology: from nanoparticles [17] to nanotubes [18] to nanorods [19].

The study of parameters influencing the transformation of anatase phase into rutileTiO_2, is important for different high-temperature processes and applications, such as gas sensors and porous membranes for gas separation [20]. This transformation sufficiently influences the properties and productivity of devices. The understanding of TiO_2 polymorphs stability, kinetics and factors influencing the phase transformations is required for the fabrication of appropriate microstructures. These aspects are critical in terms of ensuring the long-term stability of the devices.

The purpose of this study is to fabricate a thin film of TiO_2 on a silicon substrate by atomic layer deposition and investigate the phase transition in different thermal treatment modes from anatase polymorph to rutile polymorph.

2. Experiment

TiO_2 was deposited on a pre-treated silicon substrate. The substrate was a single-crystal polished plate with an orientation (111) and thickness of 350 mkm. The deposition was carried out using thermal ALD method in SI PEALD system (SENTECH Instruments GmbH). ALD is a chemical process of depositing thin films in gas phase where alternating and saturation surface reactions take place. Due to this feature ALD method can be used for deposition of precise and conformal coatings on different types of materials. One of the key benefits of ALD is its unique ability of ensuring an atomic level of films thickness and singularities control on complex geometry surfaces which is a crucial advantage of this method [21].

As initial precursors in this process we used tetraisopropyl titanate (TTIP) and deionized water (H_2O), and nitrogen as a blowout and transport gas. The graphic representation of titanium dioxide film deposition process by ALD method is given in Figure 1.

The following deposition process parameters were taken: nitrogen flow $120\,cm^3$/min, pressure in reactor ~ 60 Pa, substrate temperature — 225°C, duration of every process cycle 8 s. The process included 4 steps and was carried out in the following sequence: injection of H_2O for 1.5 s; cleaning by blowout for 3 s; injection of TTIP for 0.5 s; cleaning by blowout for 3 s. With these data the growth indicator per cycle was 0.2 nm and deposition process took

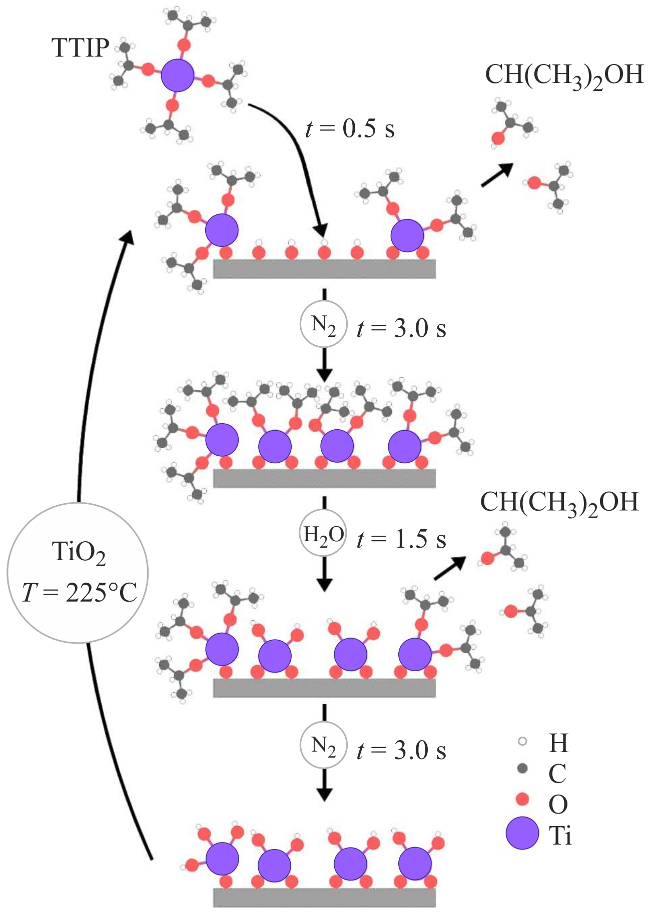

Figure 1. ALD diagram for TiO_2 deposition on silicon substrate.

7500 of these cycles. A film with thickness about 1.5 mkm was obtained finally.

As we know from the study [20], the phase transition of anatase to rutile is not instantaneous and is time-dependent since it is a reconstruction process. Therefore, for a comprehensive grasp of the phase transition kinetics we need to allow for a variety of factors influencing the temperature and time conditions. Among these parameters for the unalloyed anatase we need to take into account the shape and size of the particles, the volume of sample, heating rate, exposure time and etc. In the study [22], a method of molecular-dynamic modeling was used which helped to discover that the phase transition of pure anatase into rutile is occurs within the temperature range from 627 to 927°C. Based on these data the thermal treatment in the air under atmospheric pressure was carried out for each of the five temperatures: 600, 700, 800, 900 and 1000°C with exposure time of 1, 2 and 3 h for each temperature in SNOL muffle furnace. After every thermal treatment the samples were analyzed using an optical microscope by method of Raman scattering (RS), X-ray diffraction analysis (XRD) and atomic-force microscopy (AFM).

3. Results and discussion

In RS study of samples we used InVia Raman spectrometer from „Renishaw“, Great Britain. Spectrometer is equipped with a CCD detector with resolution $\leq 0.5\,cm^{-1}$ in visible spectrum. The RS spectra were registered within the range of wave numbers from 100 to $900\,cm^{-1}$, using Cobolt CW 532 nm DPSS laser RL532C100 with 532 nm wavelength, nominal power 100 mW, with the following parameters: lens $\times 50$, diameter of laser output spot 0.7 mm on the sample, diffraction grating with a period of 1200 lines/mm, exposure time 10 s.

As known from [3–5], anatase and rutile have a tetragonal structure with a space group for anatase — I41/amd and local symmetry C4h-19, for rutile — P42/mnm and D4h-14, respectively. In both crystals each Ti atom is surrounded by eight atoms of oxygen in the center of octahedron. In anatase each octahedron has 4 common edges, while rutile has only 2 such edges. Hence, anatase lattice cell is composed of four TiO_2 molecules, while rutile lattice cell has only two molecules. Analysis of factorial groups indicates the following optical oscillation modes for anatase: 1Ag, 1Au, 2Bg, 1Bu, 3Eg and 2Eu. Ag, Bg and Eg modes are Raman active modes, while Au and Eu are infrared active modes. Rutile is known to have four active RS conditions with symmetries B1g, Eg, A1g and B2g [4].

The RS spectra for TiO_2 film deposited by ALD, as seen in Figure 2, demonstrate the peaks at 143, 194, 392, $637\,cm^{-1}$ and a high intensity peak at $520\,cm^{-1}$. Anatase RS spectrum is known to demonstrate six active modes with peaks at 144, 194, 397, 517, 513, $639\,cm^{-1}$ [4,23,24]. The peaks at 142, 195 and $637\,cm^{-1}$ relate to Eg mode, while the peak at $394\,cm^{-1}$ relates to B1g mode. The RS line at $514\,cm^{-1}$ represents a doublet of A1g and B1g vibrational modes amplitudes. On the obtained spectrum, the high intensity peak of $520\,cm^{-1}$ relates to the silicon substrate, which overlaps the A1g and B2g symmetries of anatase corresponding to 513, $517\,cm^{-1}$. Based on data from literature [4,23,24], the RS spectrum indicates that crystalline structure of the obtained film is itself a polymorph of titanium dioxide — anatase.

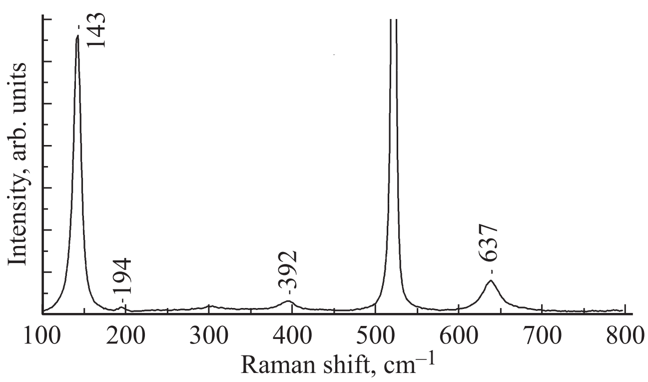

Figure 2. RS spectra of a film deposited by ALD method.

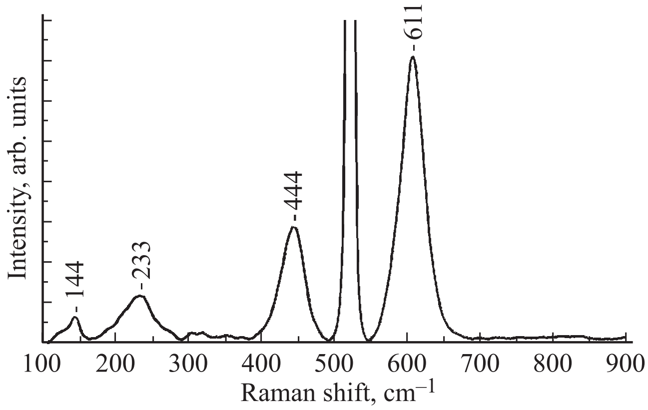

Figure 3. RS spectra of a film annealed at 1000°C for 3 h.

As known from paper [4,24], rutile has four active RS modes with symmetries B1g, Eg, A1g and B2g at 144, 243, 447 and 612 cm^{-1}, respectively. On all samples, except for the last one, that was thermally treated for 3 h at a temperature of 1000°C, the RS spectra demonstrated equivalent peaks peculiar to anatase polymorph. On the sample that was exposed for 3 h at a temperature of 1000°C, the RS spectra, as shown from Figure 3, have peaks at 143, 233, 444 and 611 cm^{-1}, and also no any distinct anatase-specific peaks are observed. The peak with high intensity at 520 cm^{-1} relating to the silicon substrate is also observed on this sample. At that, on the sample that was thermally treated for 2 h at a temperature of 1000°C, the same lattice vibrations as for the initial sample were observed, which is an evidence of a full phase transition of titanium dioxide from anatase polymorph into rutile polymorph at a temperature of 1000°C in a period from 2 to 3 h.

The X-ray structural analysis of samples performed on XRD-6100 Shimadzu diffractometer confirmed the formation of TiO_2 film of anatase polymorph resulting from deposition process. The diffraction pattern of a newly deposited sample (Figure 4, *a*) demonstrates the presence of peaks at angles that are characteristic for the lattice plane of anatase, and the absence of rutile-specific responses [3,7,20], similar for the samples thermally treated at a temperature below 900°C. The average size of crystallites defined based on the width of anatase-specific peaks with the use of Scherrer formula made about 40 nm. From the diffraction pattern in Figure 4, *b*, we see that the sample thermally treated for 3 h at a temperature of 1000°C, has very high intensity responses characteristic for rutile with planes (110) and (101), and also a low intensity peak peculiar to anatase with orientation (011). Its suggests that the phase transition process in the film has not been yet completed.

The photos of samples surfaces, shown in Figure 5, illustrate the initial and final phase transition stages. In the first photo (Figure 5, *a*) showing the surface of a sample treated for 2 h at 1000°C, we may see surface roughness and formation of re-crystallization centers, which gradually increase in dimensions. In the second photo (Figure 5, *b*), showing the surface of a sample thermally treated for 3 h at 1000°C, we may see formation of a film with a smoother surface and distinct interfaces.

From these observations we may make a conclusion that during the heat treatment the re-crystallization points are formed on the film surface and start gradually expanding in the film volume absorbing the neighboring anatase crystallites and, thus, forming the rutile film. When contacting the neighboring re-crystallized domains they do not merge and demonstrate a distinct interface.

Surface morphology of the deposited film and after phase transition were analyzed using the atomic-force microscopy SOLVER NEXT from NT-MDT Spectrum Instruments, Russia. The microscope resolution was 0.3 nm in *XY* and 0.04 nm in *Z* axis. NSG01 cantilever in a tapping mode was used for registration.

Figure 6, *a* shows the image of TiO_2 film sample surface without heat treatment where the developed structure

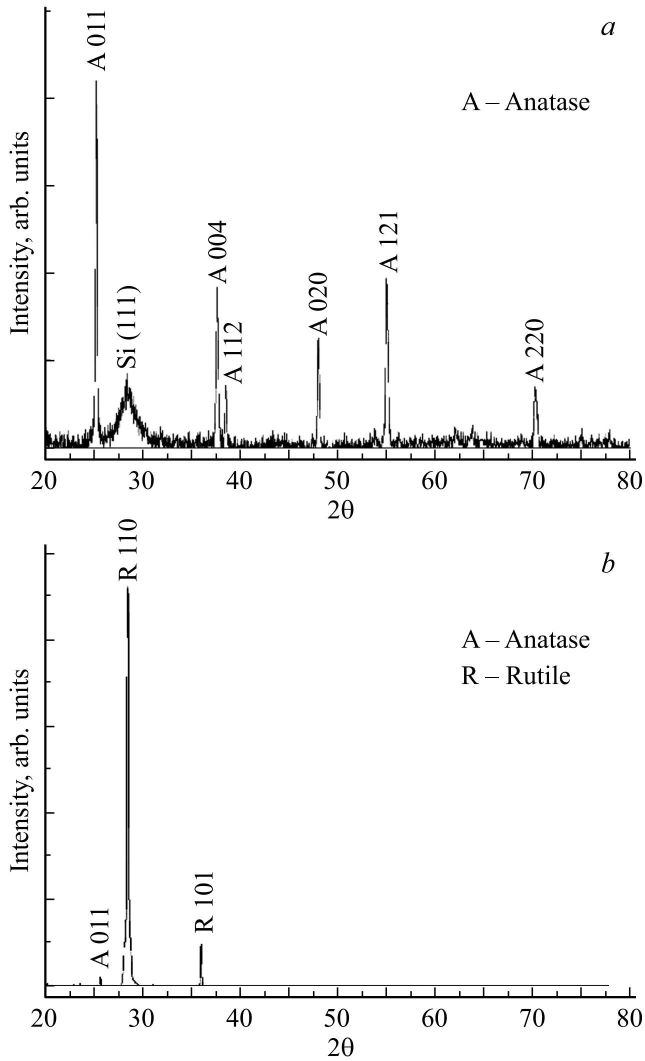

Figure 4. Diffraction patterns: *a*) for thermal treatment; *b*) after thermal treatment for 3 h at 1000°C.

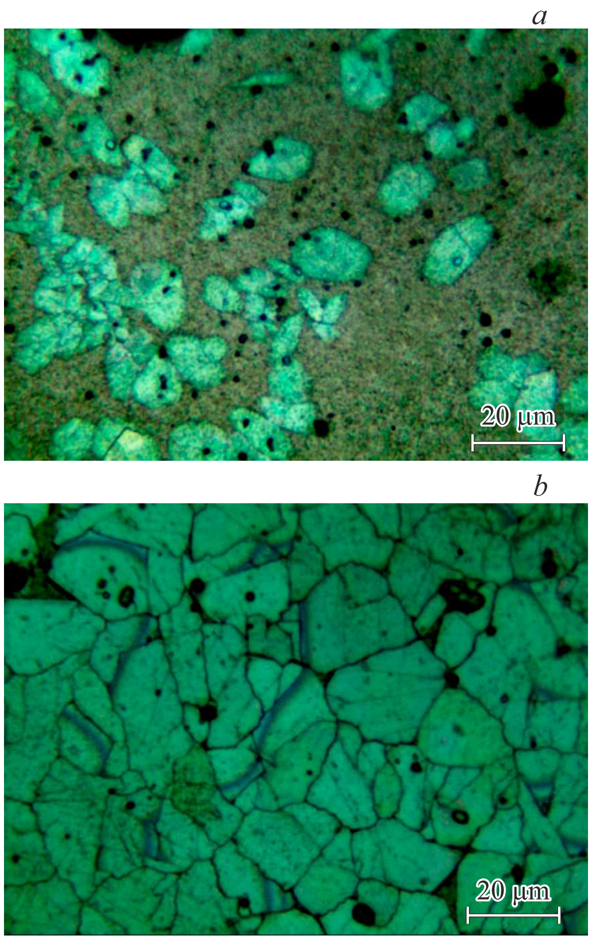

Figure 5. Photos from optical microscope: *a*) sample exposed for 2 h at 1000°C; *b*) sample exposed for 3 h at 1000°C.

composed of large polycrystalline agglomerates is distinctly seen. The same was observed for samples thermally treated up to 900°C.

The analysis of this AFM-image processes by ImageJ software demonstrated that average size of agglomerates is about 500 nm, and the grain size is about 40 nm, which is consistent with XRD analysis data. The polycrystalline morphology ofTiO_2, films obtained by ALD method suggests that Volmer-Weber type mechanism may take place during formation on the silicon substrate. This mechanism is usually observed when the generating nucleates or atoms are prone to unification or strong interaction with each other, and not with the substrate surface. As a result, random polycrystalline grains are formed that may have different orientation, as observed with TiO_2, films fabricated by ALD method. From this it follows that the film has a weak chemical bond with the substrate. This is likely to the fact, that the silicon substrate had a natural oxide film on it that served as a passivation layer and the deposition was made directly on it.

In the process of anatase-to-rutile phase transition a sufficient change of the surface structure is observed, which is can be easily seen during the analysis of both, the photos of the surface, shown in Figure 5, and the AFM-images shown in Figure 6. The polycrystalline agglomerates merge and form a film with an even and less pronounced texture; the process of the structure compaction and re-orientation into a single monolithic form takes place. The nature of the observed micro-stresses in Figure 6, *b* may be explained by both, the difference in parameters in the crystalline lattices of two polymorphous forms and the surface texture.

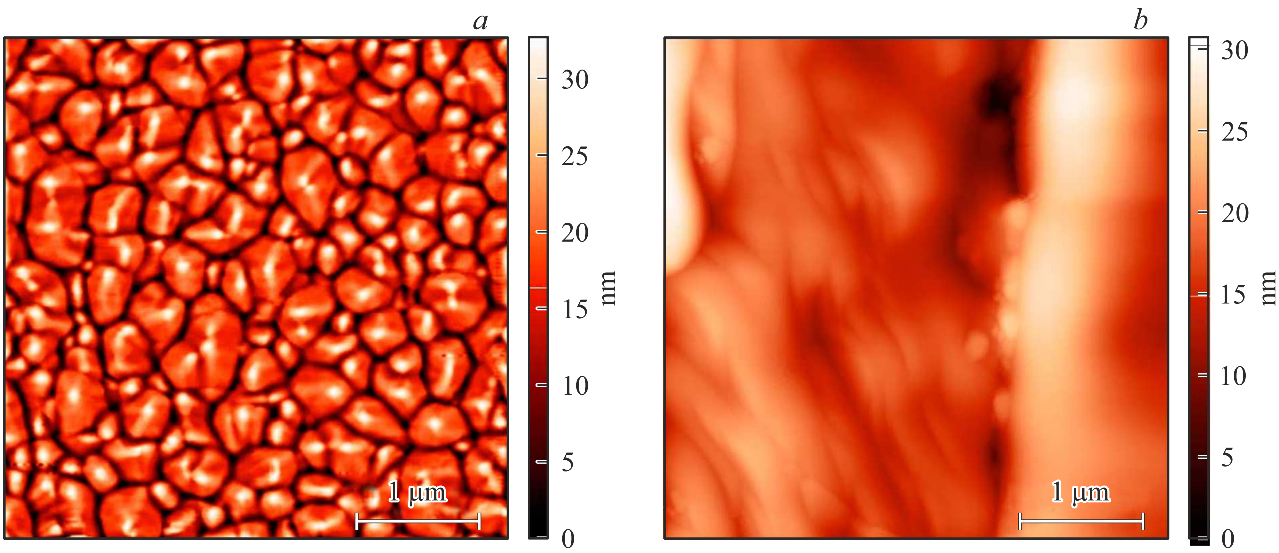

Figure 6. Images of films surfaces by AFM-mapping: *a*) non-treated sample (anatase); *b*) sample thermally treated for 3 h at a temperature of 1000°C (rutile).

4. Conclusion

Due to the structural analysis that included RS and XRD methods it was proved that when a thin film of TiO_2 is deposited on the silicon substrate by method of thermal ALD the growth of anatase polymorph is observed. The data obtained by optical microscopy, AFM and XRD methods indicate that this film is a polycrystalline structure. It consists of coarse polycrystalline agglomerates with an average size of about 500 nm and crystallites with a size of about 40 nm. This circumstance is explained by Volmer-Weber mechanism of crystallization during the film formation on a silicon substrate. This phenomenon probably occurs because of the absence of chemical bond between the precursors and the substrate at the initial process stage. Low chemical activity of the silicon substrate surface is resulting from a natural oxide film on it that serves as a passivation layer. After thermal treatment from 2 to 3 h the full phase transition of anatase to rutile in TiO_2 film 1.5 mkm thick is observed at a temperature of 1000°C. Along with that, the change in the film morphology occurs with transformation from closely-packed polycrystalline agglomerates to a more uniform monolithic structure. From these data we may make a conclusion that during thermal treatment the re-crystallization points start to occur on the film surface. These nucleates are gradually expanding within the film volume, absorbing the nearest anatase crystallites and causing the formation of rutile film. When contacting the neighboring re-crystallized domains they do not merge and demonstrate a distinct interface.

Conflict of interest

The authors declare that they have no conflict of interest.

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