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# Effect of substrate temperature on the arrangement of ultra-thin $TiO_2$ films grown by a dc-magnetron sputtering deposition

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ABSTRACT

$TiO_2$ films with a thickness between 3 and 10 nm are obtained by a dc-magnetron sputtering deposition in the reactive gas atmosphere and the properties of the films are investigated by the Raman spectroscopy, X-ray photoelectron spectroscopy and scanning probe microscopy. An influence of the deposition temperature and the post-growth annealing on the properties of the films is studied at the temperatures from 375 to 650 K. It is experimentally demonstrated that the crystalline structure can be identified by the Raman spectroscopy in the films with the thickness higher than 9 nm and annealed in the oxygen rich atmosphere for at least 2 h at about 630 K. It is proved that the changes in the film structure are not related to the changes in the chemical composition, the Ti state, and the stoichiometry of the films. Basing on the fractal analysis of topographical images, it is shown that the structural changes can be associated with the changes in the fractal dimension. These changes can be a quantitative characteristic of the structure for the films thinner than 10 nm.


## 1. Introduction

Metal oxides are extensively studied and adapted to various practical applications due to the wide possibilities to modify their electrical, catalytic and optical properties. In comparison with other oxides, the titanium dioxide seems to be the most studied material that still attracts the investigators due to a huge variety of ways for adaptation of $TiO_2$ features in the diverse areas of practical applications. Particularly high interest remains for technologies based on nanostructured materials, and among them for the deposition and properties of ultra-thin films of $TiO_2$.

Basing on technological investigations it was demonstrated that the growth of ultra-thin metal oxide films can be determined by the self-arrangement of the well-ordered structures in the limited areas on the substrate surface. In the case of physical vapour deposition (PVD), the first monolayers of $TiO_2$ films can consist of triangular islands that are dependent on the deposition conditions [1]. The annealing after the deposition can change completely the structure of the monolayers [1]. Special conditions of the PVD can lead to the nanocrystals in the form of nanoparticles, nanowires, nanorods and nanofractals of various metal oxides, including SnO, $SnO_2$, $Mn_2O_3$ and $Mn_3O_4$ [2]. On the other hand, the magnetron sputtering deposition allows producing some sophisticated ultra-thin film structures based on the composite material with the phase-separated areas, for example, n-type $TiO_2$ and p-type $Cu_2O$ in [3].

Frequently, the device development requires the materials with some specific crystalline structure. The $TiO_2$ film structure can be changed from anatase to rutile by varying the deposition pressure during the rf-plasma assistant [4] and the conventional [5] magnetron sputtering. An optimisation of the deposition temperature is another way to control the properties of the films. For this purpose, an influence of the heat treatment on the films properties has been investigated during the deposition [3,6] and after it [6,7]. The post-deposition treatment at elevated temperatures can improve the microstructure of the films [7]. In most studies, the dependence between the film properties and the formation conditions is typically investigated for comparatively thick $TiO_2$ films ($\geq$30–40 nm). The films with a thickness of about 30 nm seem to be highly sensitive to the changes in the deposition conditions [7] and their structure can significantly alter, if the thickness increases from 25 nm to 35 nm. However, the lack of detailed understanding of the relationship between the conditions of the magnetron sputtering and the ultra-thin $TiO_2$ film characteristics makes it difficult to control the features of the ultra-thin films. Therefore, our investigation is focussed on the $TiO_2$ films with a thickness in the interval of 3–10 nm.

The present report describes the experimental investigation of a relationship between the substrate temperature and the characteristics of ultra-thin $TiO_2$ films obtained by a dc-magnetron sputtering deposition. For these purposes, the substrate was kept at diverse temperatures

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during both the deposition and the post-deposition annealing. The analysis of the results is focussed on the correlation between the temperature and the changes in the surface morphology, film structure, and chemical composition.

## 2. Experimental techniques

### 2.1. Film deposition

The ultra-thin films of $TiO_2$ were obtained by a dc-magnetron sputtering deposition. For this purpose, a metallic target of pure Ti (99.995%) was sputtered in the reactive gas mixture of pure argon and oxygen with the proportion equal to 2:3. The total gas pressure was of about 6.5 Pa before and during the deposition. The deposition was performed at the constant dc-power density equal to 2.4 W/cm$^2$. Therefore, the thickness of $TiO_2$ films was dependent only on the duration of the deposition. Three groups of the films with different deposition time were produced and investigated. In Table 1, the thickness values obtained from experimental measurements are presented for each group of the films. Within each group, an individual thickness of the $TiO_2$ film was close to the typical one with an error of about ±15%. The samples from each group were investigated by all the experimental methods applied in this work. It should be noted, that there was no obvious correlation between the thickness and the parameters obtained from the experimental investigations in this work.

The films were deposited on the Si substrates with a thin $SiO_2$ overlayer. The surface of the substrates was very smooth, with the variation in the relief less than 1–2 nm. During the deposition, the substrates were kept at a constant temperature between 375 and 650 K. Several sample groups were prepared at diverse deposition temperatures. The samples listed in Table 1 were deposited at about 575 K. After the deposition, some of the samples were annealed in the oxygen-rich atmosphere at the pressure of about $10^4$ Pa for about 2 h at 630 K.

### 2.2. Material structure and chemical composition

The structure of the films was identified from the Raman spectra. Raman spectra were recorded using inVia (Renishaw) spectrometer equipped with thermoelectrically cooled (−70 °C) CCD camera and microscope. The 633 nm beam of He–Ne gas laser was used as an excitation source focused to ~ 2 μm diameter spot on the sample. The laser power at the sample was restricted to 0.5 mW. Raman scattering wavenumber axis was calibrated by the silicon peak at 520.7 cm$^{-1}$ [8]. The spectral slit width near 500 cm$^{-1}$ was equal to 4.4 cm$^{-1}$. The 50×/0.75 NA objective was used during all the measurements. Parameters of the bands were determined from the fitting the experimental spectra with Gaussian–Lorentzian shape components by using GRAMS/A1 8.0 (Thermo Scientific) software.

The surface chemical composition of the films was determined from the X-ray photoelectron spectroscopy (XPS). XPS measurements were performed in an Escalab 250Xi spectrometer (Thermo Fisher Scientific, UK) equipped with a monochromatic Al Kα source and a 6-channeltron detection system. The photoemission spectra were collected at the base pressure of $5 \times 10^{-8}$ Pa, by using 40 eV pass energy of the analyser and standard electromagnetic lens mode with about 1 mm diameter of analysed area. Dependence of the chemical composition on the sputtering depth was investigated by combining the XPS analysis and cyclic $Ar^+$ sputtering at very low energy of 0.5 keV. Spectroscopic data were processed by Avantage v.5 software. Shirley background and mixed Lorentzian/Gaussian peak shape (30%) with linked peak widths were used for the peak fitting.

The grazing angle XPS measurements for the film thickness determination were done at 40° collection angle. Before these measurements, the samples were gently cleaned by $Ar^+$ sputtering at 0.5 keV energy for 20 s, what corresponds to the removal of about 0.3 nm of the carbon contamination layer. The film thickness was calculated as a single overlayer using the Beer–Lambert law with different attenuation lengths for substrate and overlayer. The attenuation lengths were determined using the method of Cumpson and Seah [9]. The non-linear equation of the overlayer/substrate intensities ratio was solved for the overlayer thickness by using the fitting algorithm of software Avantage v.5. The results obtained from the XPS measurements for the films with individual thickness are summarized in Table 1. There were no obvious relationship between the XPS chemical composition and the deposition temperature.

### 2.3. Film morphology

Morphology of the film surfaces was visualized by a scanning probe microscope (SPM), a D3100 SPM/Nanoscope IVa (Digital Instruments) by Veeco Metrology Group. Several areas with a limited square were typically scanned in the different selected locations on the film surface of each individual sample. The SPM images of the surfaces were acquired in a non-contact tapping mode by using the probes with similar technical characteristics. In addition, the tips of the probes were classified according to the reference images obtained from the measurements of the special calibration structure from Aurora NanoDevices Inc. In these tests, the deviation of the tip parameters from that in the data sheets was obtained. In our work, we selected the probes with the tips of 8 nm radius and the deviation less than ±15%.

The SPM images of the surfaces were analysed by the methods implemented in the specialized software package, the Scanning Probe Image Processor (SPIP™ 5.1.1) of the Image Metrology A/S. In general, the square areas of the surface with the dimensions of $1 \times 1$ μm$^2$ were analysed in present study, however, also the bigger squares of $2 \times 2$ and $5 \times 5$ μm$^2$ were investigated in order to check a size influence on the results of analysis. However, the results practically were independent on the dimensions of analysed area. The two approaches were used for the analysis of the film topography. The first method is based on the statistical analysis of the SPM image. From this analysis, two characteristics, namely the distributions of height and diameter, were obtained for the grains (nanoobjects) composing the films. Diameters and heights of individual grains were calculated by the particle and pore analysis module of the SPIP from the measured shapes that were detected for the particles in the SPM topography images. The second

**Table 1**
Characteristics of the investigated samples: d-SPM is the thickness of $TiO_2$ determined by the SPM on the edge of the film, d-XPS-prof is the thickness calculated from the XPS depth profiles, d-XPS-40° is the same thickness calculated from the grazing angle XPS measurements, and O1sA/Ti2p and O1sB/Ti2p are the ratios of corresponding XPS peak areas.

| Sample | d-SPM, nm | d-XPS-prof, nm | d-XPS-40° nm | O1sA/Ti2p (as-grown) | O1sA/Ti2p ($Ar^+$ cleaned) | O1sB/Ti2p (as-grown) | O1sB/Ti2p ($Ar^+$ cleaned) |
|---|---|---|---|---|---|---|---|
| *Post-growth annealed in oxygen-rich atmosphere at 630 K* | | | | | | | |
| N1a | 5 | 5.9 | 6.5 | 2.2 | 2.1 | 0.27 | 0.31 |
| N2a | 3 | 3.1 | 3.5 | 2.2 | 2.2 | 0.39 | 0.38 |
| N3a | 9 | 11.1 | 9.5 | 2.3 | 2.2 | 0.31 | 0.26 |
| *As-grown* | | | | | | | |
| N1 | 5 | 6.3 | 6.6 | 2.2 | 2.1 | 0.28 | 0.28 |
| N2 | 3 | 3.0 | 3.5 | 2.4 | 2.0 | 0.24 | 0.36 |
| N3 | 9 | 9.8 | 9.9 | 2.3 | 1.9 | 0.32 | 0.38 |