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COMMUNICATIONS

STRUCTURAL AND MORPHOLOGICAL INVESTIGATIONS OF TiO_2 SPUTTERED THIN FILMS

Ivan Hotový [*] — Andrea Pullmannová [*] — Martin Predanocy [*] — Juraj Hotový [*] — Vlastimil Řeháček [*] — Thomas Kups [**] — Lothar Spiess [*]

TiO_2 thin films were prepared by dc reactive magnetron sputtering in a mixture of oxygen and argon on silicon and oxidized silicon substrates. The effect of post-deposition annealing (300, 500 and 700 °C for 8 h in air) on the structural and morphological properties of TiO_2 thin films is presented. XRD patterns have shown that in the range of annealing temperatures from 300 to 500 °C crystallization starts and the thin film structure changes from amorphous to polycrystalline (anatase phase). EDX measurements revealed that post-deposition annealing has affected the oxygen concentration in the film very slightly.

Keywords: TiO_2 thin films, dc magnetron sputtering, structure, morphological properties

1 INTRODUCTION

It is well known that the two crystallization phases of TiO_2, anatase and rutile, have very different optical and photocatalytic properties. TiO_2 with an anatase structure has a superior photocatalytic property compared to rutile TiO_2 while rutile shows the preferred antireflective and dielectric properties. TiO_2 has a variety of interesting applications, such as solar cells [1], as a photocatalytic material [2] as well as a gas sensor [3–7]. It is one of the most promising gas-sensing materials due to its high temperature stability, harsh environment tolerance and catalytic properties [8]. For this application, TiO_2 is used in anatase phase that features lower resistance and higher responses to gases than rutile phase, which is stable at higher temperatures. The gas-sensing properties of metal oxides are more or less related to the material surface, its high porosity and a nanostructure with small particles. Also, these properties can be essentially improved by doping of their surfaces by catalytic metals. Reactive magnetron sputtering belongs among fabrication techniques, which facilitates the control of particle properties such as size and composition on a nanometre scale, allows tight control over critical process parameters and so contributes greatly to the reproducibility of the nanostructure films.

In this study, the influence of post-annealing in the 300 to 700 °C range on the structural (XRD), composition (EDX) and morphological (AFM) properties of TiO_2 sputtered thin films was investigated.

2 EXPERIMENTAL DETAILS

The TiO_2 thin films were prepared by dc reactive magnetron sputtering from a Ti target (4 inch diameter, 99.99 % purity) at oxygen partial pressure of 0.1 Pa on both silicon and oxidized silicon substrates in a mixture of oxygen and argon. A sputtering power of 600 W was used. Both argon inert and oxygen reactive gas flows were controlled by mass flow controllers. The total gas pressure was kept at 0.5 Pa. To investigate the influence of the annealing temperature the samples were post-annealed at 300, 500 and 700 °C for 8 hours in dry air. The crystal structure was identified with a Theta-Theta X-ray diffractometer (XRD) D 5000 with a Goebel mirror in grazing incidence geometry with Cu Kα radiation. Chemical composition of the TiO_2 thin films was determined using a FEI XL30 scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyzer based on a silicon detector (EDAX) and a S-UTW-Window operating at 10 kV acceleration voltage. The surface morphology was observed by atomic force microscopy (AFM) using NT-MDT Solver under normal air conditions in the non-contact mode.

3 RESULTS AND DISCUSSION

For structural and morphological analysis, sets of as-deposited and samples annealed at temperatures 300, 500 and 700 °C were prepared. Figure 1 presents the XRD

[*] Department of Microelectronics, Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia, ivan.hotovy@stuba.sk;
[**] T. Kups, L. Spiess: FG Werkstoffe der Elektrotechnik, Institut für Werkstofftechnik, TU Ilmeau, Postfach 100565, 98684 Ilmenau, Germany

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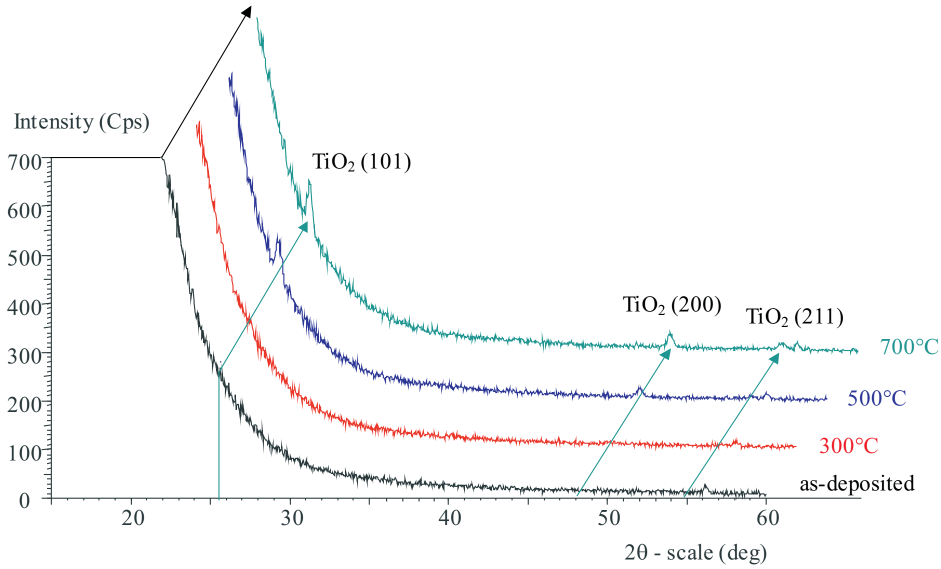

Fig. 1. XRD diffraction patterns of TiO_2 thin films as prepared and annealed at 300, 500 and 700 °C.

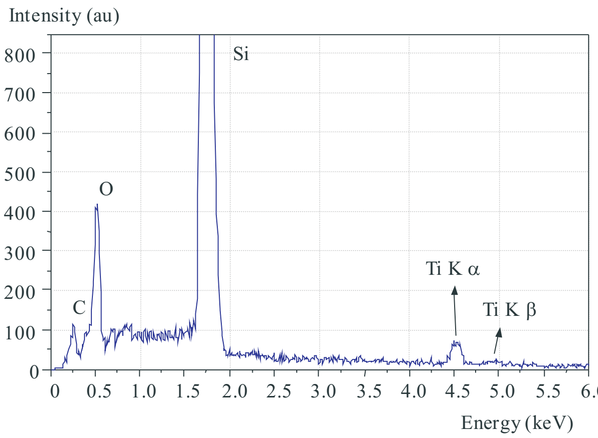

Fig. 2. Typical EDX spectrum of TiO_2 thin films.

diffraction patterns in the range of 2θ where the diffraction peaks were observed. It was found that the prepared TiO_2 films had not only an amorphous but also a polycrystalline structure. The XRD diagrams of the as-deposited and annealed at 300 °C TiO_2 films showed that the films were only amorphous, since no diffraction peaks were observed. On the other hand, the diffraction patterns from samples annealed at 500 and 700 °C show the presence of diffraction peaks from the (101) and (200) planes of the tetragonal anatase TiO_2 lattice, as referred in the PDF 00-021-1272 file. The crystallization of TiO_2 in the anatase phase is improved, as it results from the increasing of the intensity of the diffraction lines with increasing annealing temperature. Our findings are in accordance with Tian et al [9] whose XRD observation revealed that only anatase phase was formed in TiO_2 films prepared by electron beam evaporation and annealed at different temperatures. As reported in the literature [10], TiO_2 films thermally treated at temperatures below 300 °C are randomly oriented and amorphous. Gyorgy *et al* [11] also obtained TiO_2 anatase single phase thin films by pulsed laser deposition. Sicha *et al* [12] prepared TiO_2 films by dc reactive magnetron sputtering, as in our case, and found that anatase phase always was formed at low substrate temperature.

Chemical analysis of prepared TiO_2 thin films was performed by energy dispersive X-ray spectroscopy (EDX). EDX spectra were acquired from different sites of the as-prepared and the annealed samples and then were averaged. X-ray counts per second (cps) were normalized to the silicon peak in order to suppress the influence of the samples thickness and unequal measurement conditions. Besides the major $K\alpha$ silicon peak originating from the substrate, additional peaks were observed, attributed to oxygen $K\alpha$ and Ti $K\alpha$ as well as Ti $K\beta$ ones (Fig. 2). EDX spectra of all investigated samples have revealed the presence of titanium and oxygen atoms in the thin layers and thus formation of TiO_2 thin films was confirmed. The presence of carbon in the EDX spectra is due to a thin carbon film sputtered on top of the samples for SEM investigation. On the basis of comparing the intensities of O and Ti $K\alpha$ peaks of as-prepared and annealed samples, the effect of annealing on oxygen concentration in thin layers can be determined. Post-deposition annealing has affected the oxygen concentration very slightly: we observed a tendency of a small decrease of oxygen content in the layers, which can be explained by out-diffusion of oxygen during the annealing process [13]. Exact determination of Ti:O ratio is not possible since the examined TiO_2 layers are too thin and thus only a small amount of the signal acquired by EDX is attributed to the TiO_2 layer, while a major part of the signal comes from the silicon substrate.

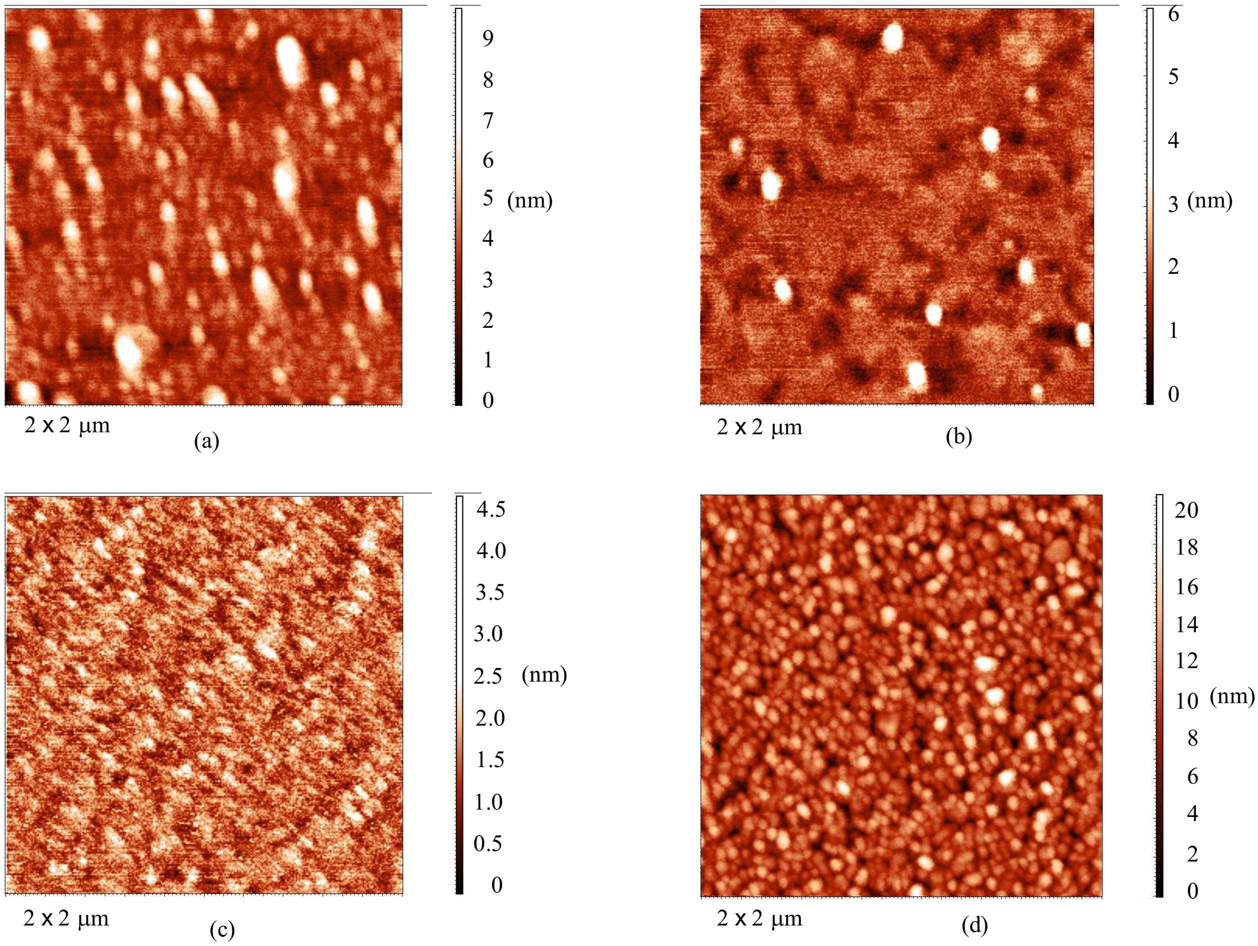

Fig. 3. AFM images of TiO_2 thin films a) as prepared and annealed at b) 300, c) 500 and d) 700 °C.

Table 1. The average of roughness ($\mathbf{R_a}$), root mean square (**RMS**) and coefficient of kurtosis ($\mathbf{R_{KU}}$) of as-prepared TiO_2 samples and annealed at 300, 500 and 700 °C

Annealing temperature (°C)	$\mathbf{R_a}$ (nm)	**RMS** (nm)	$\mathbf{R_{KU}}$ (nm)
-	0.66	0.93	3.5
300	0.32	0.46	7.9
500	0.31	0.41	0.7
700	1.90	2.46	0.6

The two and three dimensional AFM images taken at a scan area of $2\,\mu\mathrm{m} \times 2\,\mu\mathrm{m}$ (Fig. 3) represent the surface morphology of the TiO_2 thin films. After acquiring the AFM images, they were subjected to a flattening procedure using the NOVA image processing software. According to a quantitative analysis of the roughness deduced from AFM measuring (Table 1), the values of average roughness (Ra), root mean square (RMS) and coefficients of kurtosis (RKU) changed in relation to the annealing conditions. The AFM topography of the as-deposited and annealed TiO_2 films at 300 and 500 °C revealed that the film surface is rather smooth and compact (Fig. 3a-3c). From Table 1 we can see that the values of Ra and RMS of these samples follow a similar decreasing tendency. A significant difference occurs at temperature of 700 °C, where the film surface exhibits a higher roughness and clear grains can be seen (Fig. 3d). This also indicates that the grain growth on the film surface is completed at 700 °C annealing and is in accordance with the XRD observation. A quantitative roughness analysis confirmed that the process of post-deposition thermal annealing at 700 °C increased the values of Ra and RMS of the sample, indicating its good polycrystalline structure at the surface.

It was found that as-deposited samples and those annealed at 300 °C had significantly higher coefficients of kurtosis RKU, which means that these samples have infrequent extreme deviations of the measured height. This is clearly seen as spikes in the 3D picture of the samples (Fig. 3a-3b). Annealing at higher temperatures caused that these spikes were suppressed and so the samples annealed at 500 and 700 °C exhibited a surface without such spikes.

4 CONCLUSIONS

The influence of post-annealing (300, 500 and 700 °C for 8 h in air) on the properties of TiO_2 sputtered thin films was investigated. The annealing of the TiO_2 films has an important effect on the thin film structure; in particular, crystallization starts at temperatures between 300 °C and 500 °C without diffusion of oxygen. This process has a significant influence on the structural and morphological properties of TiO_2 thin films. EDX measurements revealed that post-deposition annealing has affected the oxygen concentration in the film very slightly. The AFM topography of the as-deposited and annealed films at 300 and 500 °C showed that the film surface is rather smooth and compact. A significant difference occurs at temperature of 700 °C, where the film surface exhibits a higher roughness and clear grains were observed. Further studies are in progress to show the sensing properties and their improving by means of doping with different elements.

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Ivan Hotový received his MSc in Electronics from the Slovak University of Technology in Bratislava in 1982 and his PhD in Electronics from the Slovak University of Technology in 1994. He is a scientific worker and lecturer at Department of Microelectronics, FEIT STU. His current research interests include the development of gas sensors, magnetron sputtering of metal oxide films and plasma etching of compound semiconductors.

Andrea Pullmannová received her MSc in Microelectronics from the Slovak University of Technology in Bratislava in 2006. Her current interest is concern to electrical characterization of gas sensing structures based on thin metal oxide films.

Martin Predanocy received his MSc in Microelectronics from the Slovak University of Technology in Bratislava in 2009. He is a PhD student in Department of Microelectronics, FEIT STU. His current research interests include characterization of electrical, optical and structural properties of gas-sensing materials and the development of gas sensors.

Juraj Hotový received his MSc in Microelectronics from the Slovak University of Technology in Bratislava in 2009. He is a PhD student in Department of Microelectronics, FEIT STU. His current research interests include the characterization of electrical, optical and structural properties of transparent conductive oxides for solar cells application.

Vlastimil Řeháček received his MSc in Nuclear Chemistry from the Comenius University in Bratislava in 1982 and his PhD in Electronics from the Slovak University of Technology in 2005. He is a scientific worker in Department of Microelectronics, FEIT STU. His current research interests include the development of voltammetric sensors, gas sensors and photolithography.

Thomas Kups received his Diploma in 2001 in the Department of Physics and his PhD in 2006 in the Department of Physics and Astronomy from the Friedrich-Schiller-University Jena, Germany. Since 2006, he is a scientific researcher at the Technical University Ilmenau. His recent research focuses on the transmission electron microscopy investigations of III-Nitrides, metal-oxides and SiC.

Lothar Spiess is a Proffessor at Department of Materials Technology, Technical University of Ilmenau. His interest is concern to material microanalysis and semiconductor processing.