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Influence of substrate type and its placement on structural properties of TiO_2 thin films prepared by the high energy reactive magnetron sputtering method

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The paper presents studies of the influence of substrate type and its placement on structural properties of TiO_2 thin films prepared by the high energy reactive magnetron sputtering method. During the deposition, conditions of the magnetron powering have been especially selected to enhance the nucleation energy. Thin films were deposited on Si(100) and SiO_2. Substrates were placed on a plate at three distances from the centre of the target. Selected substrates were also placed under various angles with respect to the plate. Thin films were examined using X-ray diffraction (XRD) and atomic force microscopy (AFM). XRD analysis showed existence of TiO_2-rutile phase with preferred (110) orientation and AFM measurements revealed nanocrystalline structure of the films.

Key words: *TiO_2; thin films; reactive sputtering; structural properties*

1. Introduction

Due to its optical, electrical and chemical properties, TiO_2 has been one of the most intensively studied metal oxides in the recent years. Though TiO_2 can exist in three different phases (brukite, anatase, rutile), only rutile is thermodynamically stable at ambient conditions. TiO_2 thin films can be amorphous, polycrystalline or mixed, depending on the deposition method. Another very important factor is crystallite size. It has been reported that oxides with grains in the range of nanometers (less than 100 nm) possess a lot of unique properties [1]. Such nanocrystalline materials can be used for new applications in sensors, photodetectors, nanotransistors, solar cells, optical

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coatings, switches and modulators [2]. That is why structural properties of titanium dioxide and their correlation with methods of their fabrication are of great interest. Magnetron sputtering [3] is one of numerous techniques applied so far to deposit TiO_2 thin films.

In this work, influence of substrate type and its placement on structural properties of TiO_2 thin films have been presented.

2. Experimental procedure

Thin films were prepared by the high energy reactive magnetron sputtering (HE RMS) method using Ti target [4]. During the deposition, special conditions of the magnetron powering have been selected to enhance the nucleation energy. Prepared thin films exhibited highly ordered nanocrystalline structure. Thin films were deposited on Si(100) and SiO_2. Substrates were placed on a plate with special tilted and hemispherical holders in three zones from the centre of the target (Fig. 1).

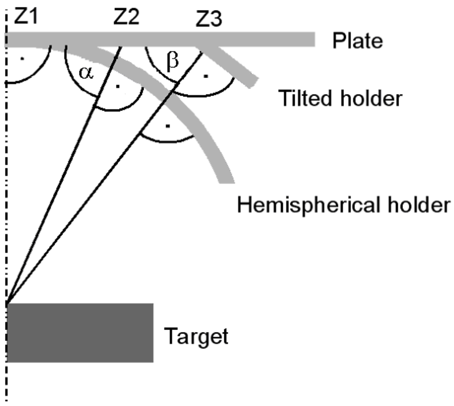

Fig. 1. Side view of a plate with special tilted and hemispherical substrate holders in the deposition process of TiO_2 thin films; Z1, Z2, Z3 – internal, medium and external zones, respectively

Structural properties were investigated by means of X-ray powder diffraction (XRD), performed using DRON-2 powder diffractometer with Fe-filtered CoK_{α} radiation. Average size of crystallites was calculated from XRD spectra in a conventional way according to the Scherrer formula [5]. The topography was studied using atomic force microscope (AFM) (Veeco PicoForce) working in a contact mode.

3. Results and discussion

All examined thin films revealed the existence of TiO_2-rutile phase (Tables 1, 2). In Table 1, dependences of structural parameters of TiO_2 thin films on the substrate inclination angle and distance from the target in the deposition process, placed in Z3 with base cut perpendicular (⊥) to plate radius have been presented. The analysis shows that preserving constant distance to the plate radius and decreasing the substrate (S1, S2) inclination angle (α, β) results in increasing the difference between the interplanar distances (Table 1). The grain size *D* does not change.

Table 1. Dependence of structural parameters of TiO_2 thin films on the substrate inclination angle and distance from the target in deposition process; base cut perpendicular (⊥) to plate radius*

Sample	Substrate	Zone	Placement	Phase	D [nm]	d [nm]	d_{PDF} [nm]	$d - d_{PDF}$ [nm]
S1	Si(100)	Z3	plate	rutile	7.9	0.3268	0.3247	tension 0.0028
S2			tilted holder		7.8	0.3255	0.3247	tension 0.0008
S3			hemispherical holder		6.7	0.3247	0.3247	relaxation 0
S4	SiO_2		hemispherical holder		8.7	0.3250	0.3247	tension 0.0003

*D – grain size (nm), d – interplanar distance (nm), d_{PDF} – interplanar distance (nm) from PDF file [6].

Table 2. Dependence of structural parameters of TiO_2 thin films on base cut placement relative to plate radius*

Sample	Substrate	Zone	Placement	Base cut	Phase	D [nm]	d [nm]	d_{PDF} [nm]	$d - d_{PDF}$ [nm]
S5	Si(100)	Z2	hemispherical holder	⊥	rutile	5.6	0.3259	0.3247	tension 0.0012
S6				||		5.8	0.3242	0.3247	compression –0.0005

D – grain size (nm), d – interplanar distance (nm), d_{PDF} – interplanar distance (nm) from PDF file [6].

Concurrently, decreasing the distance to the plate radius and substrate inclination angle results in a decrease of grain size (S1, S2). On the hemispherical holder (S3, Table 1), the structure of thin film becomes relaxed ($d - d_{pdf} = 0$) and the grain size smaller. The grain size of the film deposited on SiO_2 is ca. 30% larger than that of deposited on Si in the same zone (Z3), (S4, Table 1).

In Table 2, a dependence of structural parameters of TiO_2 thin films (in Z2) on the placement of the base cut relative to the plate radius has been presented. It can be seen that the grain size is closely the same for both samples (S5 and S6). However, in the case of parallel (||) placement of the base cut with respect to the plate radius, the film was compressed compared to the PDF value (S6, Table 2) contrary to perpendicular (⊥) placement, in which thin films were tensed compared to PDF.

Figures 2 and 3 present AFM images of TiO_2 thin films on Si(100) placed on a hemispherical holder in Z2 with the base cut parallel (||) and perpendicular (⊥) to the plate radius, respectively. AFM images confirm nanocrystalline structures of the films. As can be seen, the grains have the same dimensions and a higher degree of ordering can be seen in the case of sample S6 (Fig. 3).

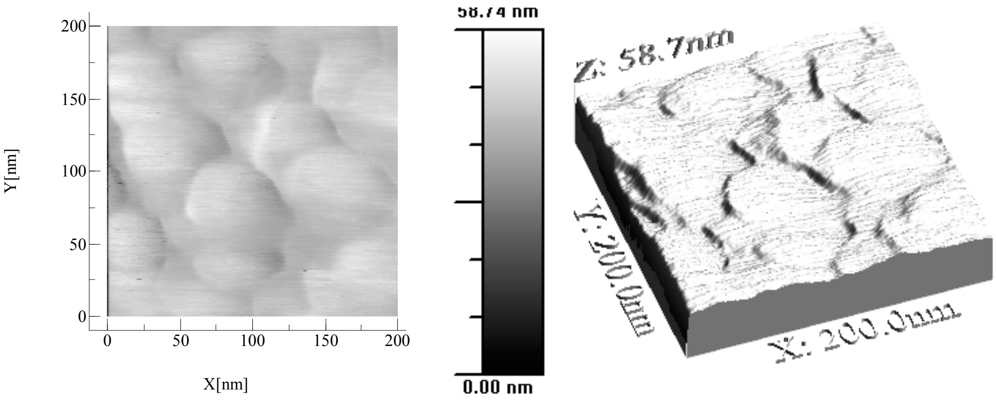

Fig. 2. AFM images of TiO_2 thin film on Si(100) placed on a hemispherical holder in Z2; base cut perpendicular (⊥) to plate radius (sample S5)

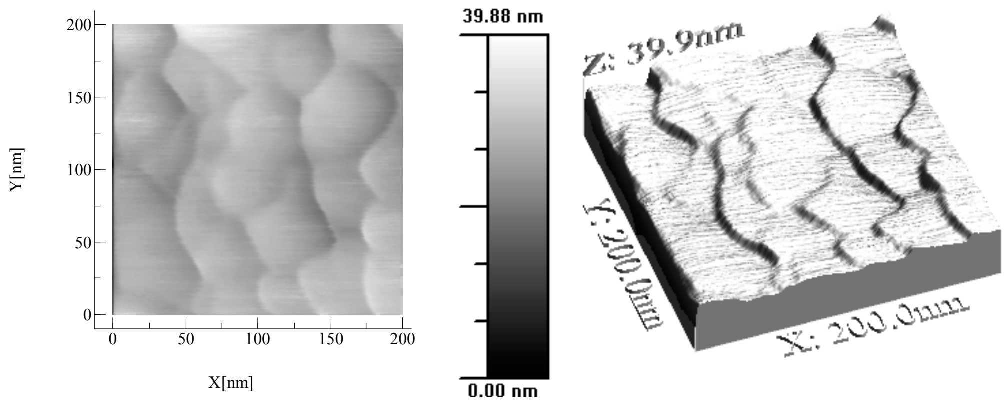

Fig. 3. AFM images of TiO_2 thin film on Si(100) placed on a hemispherical holder in Z2; base cut parallel (||) to plate radius (sample S6)

4. Conclusions

The type of used substrates (monocrystalline, amorphous) as well as the way of their placement with respect to the target have the influence on the structure of TiO_2 thin films. The sizes of TiO_2 nanocrystalites on SiO_2 substrate are on average larger by about 30% in comparison to the grain sizes of those deposited on Si. Substrate placement with respect to the target (distance and angle) influences the grain size as well as the compression of the examined TiO_2 thin films.

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