Research Article

Photocatalytic Activity of Nanostructured Titanium Dioxide Thin Films

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Received 29 April 2012; Revised 17 June 2012; Accepted 1 July 2012

Academic Editor: Panagiotis Lianos

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The aim of this paper is to investigate the properties and photocatalytic activity of nanostructured TiO₂ layers. The glancing angle deposition method with DC sputtering at low temperature was applied for deposition of the layers with various columnar structures. The thin-film structure and surface morphology were analyzed by XRD, SEM, and AFM analyses. The photocatalytic activity of the films was determined by the rate constant of the decomposition of the Acid Orange 7. In dependence on the glancing angle deposition parameters, three types of columnar structures were obtained. The films feature anatase/rutile and/or amorphous structures depending on the film architecture and deposition method. All the films give the evidence of the photocatalytic activity, even those without proved anatase or rutile structure presence. The impact of columnar boundary in perspective of the photocatalytic activity of nanostructured TiO₂ layers was discussed as the possible factor supporting the photocatalytic activity.

1. Introduction

Titanium dioxide is one of the most investigated materials in the last decades. Three forms of TiO₂ can be found in nature: anatase, rutile, and brookite. Its properties like a high refractive index, chemical and mechanical stability, and/or photocatalytic activity [1–3] predetermine this material for a wide range of applications.

One of the most attractive areas concerning titanium dioxide is its photocatalytic activity. The photocatalytic effect of TiO₂ material is based on generation of electron-hole pairs due to the UV irradiation of TiO₂. The generated pairs diffuse to the surface of the material and participate in the surface reaction leading to the decomposition of adsorbed matter [2].

A lot of articles have been published about the relation between the thin-film structure and the photocatalytic activity [4–6]. Generally, the presence of anatase or its mixture with rutile has been reported as an assumption for the photocatalytic activity of titanium dioxide films. The rutile acts as an antenna extending the photoactivity into visible wavelengths, and the structural arrangement of the similarly sized TiO₂ crystallites creates catalytic “hot spots” at the rutile-anatase interface [7–10].

One of the most important factors affecting the photocatalytic efficiency is the lifetime of the electron/hole pairs. The excitons generated during the UV irradiation of TiO₂ layers dissipate the stored energy within few nanoseconds by the recombination. Doping of the thin-film surface leads to enhancement of the excitons lifetime (as

well as photocatalytic activity) because of a Schottky's barrier creation [11, 12]. Similarly, the existence of the grain boundary in TiO_2 material also enhances the photocatalytic reaction [13]. The explanation of this effect is related to bending of energetic bands. The bent bands around grain boundaries tend to separate the electrons and holes resulting in enhancement their lifetimes.

TiO_2 photocatalytic films can be prepared by various methods of which SOL-GEL, PECVD, and/or PVD belong to the most frequently used. One of the well-available PVD technologies enabling the deposition of thin films with columnar structure is the so-called glancing angle deposition. (GLAD) [14–16]. This method is based on variation of the incident particle angle to the substrate as schematically shown in Figure 1. The variation of the incident angle enables formation of nanostructured films with oriented columnar structures.

The presence of columnar structure and architecture type of columns strongly affect functional properties of thin films [18–20]. The aim of our investigations was to study the impact of an oriented structure on the photocatalytic activity TiO_2 layers.

2. Experimental Section

TiO_2 films were deposited in a classical PVD apparatus equipped with a movable substrate nonheatable holder. Changing the angle of the holder and/or its rotation enables the control of the film columnar structure. The detailed description of the experimental setup has been described elsewhere [14].

The ultimate pressure inside the chamber was about 1 Pa; typical values of discharge current and voltage were 200 mA and 450 V, respectively. Argon with the admixture of oxygen was used as a working gas mixture. The oxygen was flowed either constantly of 2 sccm (reactive gas constant flow—RGCF) or in a pulsed mode (reactive gas pulsing process—RGPP). The period of the pulsation was 45 s with the $t_{\text{on}} = 27$ s and $t_{\text{off}} = 18$ s.

The amount of the injected oxygen during the t_{on} of RGPP was two times higher than the amount of the constantly injected oxygen into the chamber during RGCF. The reason for this was to reach the same stoichiometry of the layers— TiO_2 . The same stoichiometry of deposited layers was proved by ESCA analysis.

The surface morphology of thin films was investigated by the atomic force microscopy (AFM) and scanning electron microscopy (SEM). Nanoscope 3 MORTIMORT machine was used for the AFM. Surfaces of all the samples were scanned by the contactless regime using the FastScan method with resonance frequency 50 kHz. The software Gwyddion was used for the evaluation of the arithmetic roughness calculation. The values of the arithmetic roughness were evaluated due to the comparison of AFM data matrix by the middle plane interlay. The values of the arithmetic roughness indicate the arithmetic deviation from a mean value of point heights.

FIGURE 1: Principles of glancing angle deposition [17].

The JEOL-JSM 740 scanning electron microscope operated with accelerating potential 5 kV and working distance of 14.4 mm.

The thin-film structure was investigated by the X-ray diffraction. Due to a low value of the thin-film thickness, the special diffractometer X'Pert Pro made by the PANalytical company was used with $\text{CoK}\beta$. The Göbel mirror was placed into the way of an incident beam. The angle of the beam incidence was 3° .

For the determination of the ratio of specific surface P to nominate surface P_0 the method based on the sorption of krypton was performed. Sorption measurements of porous thin films were carried out at the temperature of 77 K. Micromeritics ASAP 2010 was used for the Krypton volume adsorption measurements. The P/P_0 ratio was calculated from the measured lines using the basis of BET analysis. The method is described in detail in [21].

The photocatalytic activity was derived from the decomposition speed of aqueous solution of the Orange 7 (sodium salt of sulphonated azo dye), assuming the Langmuir-Hinshelwood law for degradation according to the pseudo-first-kinetic order. The experimental method and determination of the apparent kinetic constant K_{app} in full details described in paper [22]. This kinetic constant K was normalized to the UV irradiation intensity (W/m^2), the volume of AO7 solution (m^3), and the area of irradiated TiO_2 layer (m^2).

The photocatalytic activity of the deposited films was also compared with the films prepared from commercially available Evonik/Degussa Aeroxide P25 photocatalyst. Samples in form of this powder were prepared by sedimentation on soda lime glass substrates. The sedimentation was performed by placing $0.2 \text{ mL}/\text{cm}^2$ of aqueous suspension of known catalyst concentration on the substrate, followed by drying. After the drying process under laboratory condition, the deposited layers were heated to 300°C for 30 minutes to achieve the better adhesion of the particulate layer on the glass support. Such prepared layers contain 0.5 mg of P25 per cm^2 , with layer thickness of 5 microns. The efficiency of Degussa Aeroxide P25 is shown only for the comparison of TiO_2 films made by PVD GAD with highly efficient photocatalyst.

FIGURE 2: SEM analyses of chosen thin-film edges.

3. Results and Discussion

Four types of the thin-film structure were prepared in dependency on GLAD parameters (a deposition angle α and rotation angle Φ ; see Figure 10)—dense layer and three columnar structured types of the thin films: incline, zigzag and helical columns (see Figure 10).

Both the RGCF and RGPP methods were applied for deposition of each type of the structure, presented in Figure 10. The thickness of all the layers was approximately 200 nm. The SEM pictures of edge fracture are presented in Figure 2.

The thin films called dense layers (Figures 2(a) and 2(e)) were deposited with the substrate placed perpendicularly to the particle flow (parallel to the target—the most frequently used method for PVD) and without any substrate rotation. The results of the SEM analysis for this type of the deposition are in a good agreement with Thornton's thin-film growth model defining so-called T-zone [23]. This zone is typical for its dense and fiber-like grain, in which the grain outlines are difficult to identify, which can be seen in Figures 2(a) and 2(e) (see circles). The layers called incline (Figures 2(b) and 2(f)), zigzag (Figures 2(c) and 2(g)), and helical columns (Figures 2(d) and 2(h)) clearly show the columnar structure corresponding to the glancing angle deposition parameters. The individual columns are in the mutual contact, so the hypothesis of the columnar boundary presence is proved by this analysis.

The surface morphology was investigated by SEM and AFM analysis. The SEM pictures of surfaces of particular samples are shown in Figure 3.

The surface of dense layers (both RGCF and RGPP: Figures 3(a) and 3(e)) proved the smoothest surface in comparison to the oriented structured thin films (incline/zigzag/helical columns). Dense layers (both RGCF and RGPP) are typical for the absence of a global shape formation (see Figures 3(a) and 3(e)) which can be seen on the surfaces of the rest of the analyzed samples (see Figures 3(b), 3(c), 3(d), 3(f), 3(g), and 3(h)). For both deposition methods, thin films with incline columnar structure proved the presence of a global shape formation with diameter in the limits between 20 nm and 60 nm (see Figures 3(b) and 3(f)). The layer with zigzag columnar structure made by RGCF showed smooth surface with poor presence of a global shape formation with diameter in the limits 10 nm and 30 nm (see Figure 3(c)), whilst the same structured thin film made by RGPP proved the rich presence of such grain formation with diameter up to 100 nm (see Figure 3(g)). From the point of view of deposition method, similar results in surface differences were observed for thin films with helical-column structure. The layer made by RGCF showed the presence of a global shape formation with diameter approximately 20 nm (see Figure 3(d)) whilst the layer made by RGPP proved the rich presence of grains with diameter in the limits 50 nm and 100 nm (see Figure 3(h)). Figure 3 demonstrates that that layers made by RGPP proved evidently more diverse

FIGURE 3: SEM surface photos.

structure of surfaces in comparison to the surfaces of the thin films made by RGCF.

To quantify the differences in the thin-film surface structure, the arithmetic roughness measurement by AFM was evaluated and the arithmetic roughness for was calculated for all the samples. Results are summarized in Figure 4. Each value represents average value of 5 independent measurements.

The lowest value of the arithmetic roughness was observed at the dense layer made by RGCF—1.6 nanometers. The layer with zigzag columns made by RGPP showed the highest value of the arithmetic roughness—3.9 nanometers. Higher values of the arithmetic roughness observed at the layers with the oriented structure (incline, zigzag, and helical columns) are clearly visible in comparison with the nonoriented structured layers (dense layers). This is in a good agreement with the SEM surface analysis shown in Figure 3, where the dense layers proved the smoothest surface in comparison to the oriented structure layer.

The pulsation of the reactive gas is known to reduce the target poisoning resulting in higher sputtering yield. The higher deposition rate during the RGPP in combination with moderate sputtering of the substrate during the oxygen off-phase might be the reason of generally higher surface roughness of samples prepared by RGPP in comparison with those deposited by RGCF.

FIGURE 4: Roughness in dependency on layers structure.

High specific surface is a general assumption for effective catalytic reaction. Jong [24] reported the increased photocatalytic activity with larger specific surface of titanium dioxide thin films. The specific surface was determined by the krypton sorption method on selected samples. An example

FIGURE 5: Dependency of adsorption on relative pressure during Kr adsorption.

FIGURE 6: Specific surfaces of TiO_2 layers.

of a typical measured absorption curve is in Figure 5. The quantitative values of the specific surfaces P normalized to the nominated surface P_0 are summarized in Figure 6.

The normalized specific surface P/P_0 of the films with oriented structure is substantially higher than the P/P_0 of the non/structured films. The layers with the oriented structure proved also higher arithmetic roughness in comparison with nonoriented thin films. The most probable explanation of these results is based on the hypothesis that columnar structure enhances the pores forming which could positively affect the sorption, and so the high values of P/P_0 could be observed at the thin films with oriented structure, especially the most pronounced for the layer with helical type of columns deposited by RGPP. This layer has 60 times higher value of P/P_0 ratio than the dense layers.

FIGURE 7: Results of low-angle XRD for layers made by RGCF.

FIGURE 8: Results of low-angle XRD for layers made by RGPP.

To the investigation of crystalline quality, low-angle X-ray diffraction analysis was realized on the individual representatives for each type of the structure and both deposition methods. In Figure 7 results of this investigation are shown for layers made by RGCF; in Figure 8 X-ray diffraction results are shown for RGPP deposition method.

It is obvious from Figures 7 and 8 that layers with the helical structure (both RGCF and RGPP) seem to be amorphous (exactly the crystalline formation is below the resolution limit of the used method which is 3 nm).

Mostly the presence of the anatase structure (angle values— 29.9° , 57.3° , 74.9°) was proved by the low-angle XRD for incline and zigzag column architecture type (both RGCF and RGPP), especially anatase peaks relevant to the angle 29.9° . Rutile phase is proved by the peak with low intensity at the angle value equal to 51.6° .

The normalized kinetic constants r in dependency on the layer structure are presented in Figure 9. The kinetic constant r for Aeroxide TiO_2 P25 Degussa layer (with thickness approximately $5 \mu\text{m}$) is also displayed.

FIGURE 9: Photocatalytic activities in dependency on thin-film structure.

The dark absorption measurement was part of the photocatalytic activity analysis. All tested samples were immersed in the AO7 solution in the dark for 6 hours. The AO7 concentration changes were evaluated due to UV/VIS spectroscopy, and no differences between the initial and final concentration were observed, even for films with different values of the specific surface area (Aeroxide TiO₂ P25 Degussa). Based on these results, the contribution of dark absorption to the AO7 concentration decrease was excluded.

All tested samples were irradiated by UV for the same time of 6 hours and only the initial and final concentrations were analyzed. According to our experiences with this type of experiments and results presented in [25–27], the dependence of AO7 decomposition on the time of irradiation has a decreasing exponential character.

Figure 9 summarized the obtained reaction constants. All the samples evidence photocatalytic activity in the limits between $2 \cdot 10^{-5} \text{ m}^3 \text{ h}^{-1} \text{ W}^{-1}$ and $5.4 \cdot 10^{-5} \text{ m}^3 \text{ h}^{-1} \text{ W}^{-1}$. The highest value of r was reached with the incline-columned layers reaching up to 70% of Aeroxide TiO₂ P25 Degussa efficiency.

As mentioned above, the photocatalytic activity is connected with presence of anatase or anatase/rutile crystalline fractions (Figures 7 and 8). The peaks with highest intensity relevant for both the anatase and rutile were found for the dense layers. Thus these films, in comparison with the other layers, contain anatase/rutile crystalline structure. However, these layers evidence the lowest photocatalytic activity of all the investigated samples.

On the other hand, the films with helical-columns structure evidence substantial photoactivity even though they did not prove any crystalline phases. The dense layers should exceed the photocatalytic activity of the thin films with helical-column structure due to the positive impact of the crystalline anatase/rutile phases [28–30]. However, from Figure 9 the comparable values are obvious, both for the dense- and oriented-structured layers.

The high value of the specific surface area connected to the layer with helical columns made by RGPP should be one of the factors explaining the comparable photocatalytic activity of amorphous helical-column layers with dense layers proving the presence of anatase and rutile. On the other hand, from Figure 6 it is obvious that the specific surface area of the layer with the helical columns made by RGCF is approximately two times lower than the layer with the helical columns made by RGPP. However the layer made by RGCF proved a higher photocatalytic activity than the layer deposited by RGPP (Figure 9). The value of ratio P/P_0 for zigzag column layer made by RGPP is almost two times lower than that for the layer with helical columns made by RGPP, but the photocatalytic activity of zigzag layer is more than two times higher. Thus the factor of the specific surface area could not unambiguously explain the high photocatalytic activity of the nanostructured films.

As already mentioned above, the photocatalytic effect of the TiO₂ is connected with anatase/rutile structure and amorphous phase is swallowed to be detrimental in pure TiO₂ photocatalyst. On the other hand Horakova et al. [11] have found that incorporation of Ag nanoparticles into the bulk of amorphous TiO₂ film also results in substantial enhancement of their photocatalytic activity. Enhancement of the photocatalytic efficiency due to the formation of metal nanoparticles on the surface of photocatalytic anatase films was proved by several authors [2, 22]. These particles form a metal/semiconductor junction acting as an electron trap resulting in the life-time enhancement of the electron-hole pairs. Kamei [13] reported direct observation of grain-boundary effect on the photocatalytic activity of bicrystalline rutile TiO₂. This article proved that the existence of the grain boundary in TiO₂ crystal enhanced the photocatalytic reactions. The authors of that article assumed that around the boundary the bending of band gaps is realized, leading to the enhancement of the electron-hole life-time due to the electron capture. Thus presence of some kind of boundary (Schotky's barrier—metal/semiconductor boundary; crystalline phases/amorphous phases boundary; grain boundary) results in the improvement of the TiO₂ photocatalytic activity. We believe that the columnar structure formation (in fact the boundary formation due to the mutual contact of individual columns) is one of the factors leading to the observed photocatalytic efficiency of the amorphous nanostructured films due to enhancement of the electron-hole pairs (excitons) lifetime due to the electron-hole separation on the columnar boundary of the oriented structured layers.

4. Conclusion

TiO₂ thin films were prepared by the GLAD PVD method. The films evidenced nanostructured columnar structure. They are characterized by higher surface roughness and substantial higher specific surface in comparison with films prepared by conventional PVD. All the films evidence photocatalytic activity even those with amorphous character. Boundaries between the oriented structures are explained to be a reason of the photocatalytic activity of amorphous TiO₂

Type of architecture	Normal angle α (°)	Rotation angle Φ	
Dense layer	0	No rotation during the deposition	
Incline	80	No rotation during the deposition	
Zig zag columns	80	Rotation 180° in the plane of the substrate every 30 minutes	
Helical columns	80	Rotation 90° in the plane of the substrate every 15 minutes	

FIGURE 10: GLAD parameters relevant to specific structure.

layers. The photocatalytic activity was observed at the thin film with zigzag columnar structure made by RGPP reaching 70% efficiency of Aeroxide TiO₂ P25 Degussa.

Acknowledgments

This work was supported by MSMT, Project NANOPIN 1M0577, by GA AV CR, Project No. KAN101120701, and by the project CZ.1.05/2.1.00/03.0086 funded by European Regional Development Fund.

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