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Ceramics International 39 (2013) 2787–2794

CERAMICS INTERNATIONAL

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Photocatalytic activity of thin TiO_2 films deposited using sol–gel and plasma enhanced chemical vapor deposition methods

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Received 6 July 2012; received in revised form 14 September 2012; accepted 14 September 2012
Available online 23 September 2012

Abstract

Thin titanium dioxide films, deposited using RF PECVD and sol–gel techniques, were studied comparatively with respect to their bactericidal as well as self-cleaning properties. The effect of the deposition process on film morphology, chemical and crystalline structure, bactericidal activity and hydrophilic properties was investigated using scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), surface profilometry, optical microscopy and contact angle measurements. It was found that the bactericidal activity of amorphous TiO_2 films, produced using the RF PECVD method, as either comparable to or better than those of crystalline (anatase) films deposited by means of the sol–gel technique. One reason for such advantageous behavior of plasma deposited materials is thought to be their substantially higher surface roughness, as revealed by AFM measurements. The hydrophilic effect, induced with UV irradiation, was strongest in the case of sol–gel films, but the RF PECVD synthesized coatings were found to be only slightly less hydrophilic. The conclusion follows that both sol–gel and RF PECVD techniques are equally capable of producing titanium dioxide films of high photocatalytic quality.

Keywords: D. Titanium dioxide; A. Sol–gel processes; RF PECVD processes; Photocatalytic activity

1. Introduction

Among many applications of titanium dioxide (titania, TiO_2), there are quite a number belonging to the high-tech category and these make use of the photocatalytic properties of this material. Such applications as water and air sterilization or their purification from organic and non-organic pollutants are being broadly tested and developed [1–6]. The photocatalytic properties of titania are evidenced by the ability of thin coatings of this material to exhibit disinfecting activity following their illumination with UV light [7,8]. These properties make the material a good candidate for such applications as medical devices, food preparation surfaces, sanitary coatings, etc. Photogenerated properties also include the superhydrophilic effect, consisting in a substantial lowering of water contact angle under the exposure to UV radiation. Transparent superhydrophilic TiO_2 films deposited onto glass substrates may be used in such practical applications as antifogging and self-cleaning surfaces [9–11].

Among stable polymorphic forms of TiO_2, anatase appears to have the strongest potential for photoinduction, while rutile is thought to be less effective [1–14]. The amorphous phase, on the other hand, was long considered incapable of inducing the photocatalytic effect and consequently of obliterating microorganisms and oxidizing organic and inorganic compounds. In a few reports, however, it was shown to exhibit the photowetting effect [15–16].

TiO_2 coatings can be prepared by a number of deposition techniques, such as the sol–gel process [3,16–19], reactive sputtering [10,13], chemical vapor deposition [20], spray pyrolysis [21], or plasma enhanced chemical vapor deposition (PECVD) [22–24]. Due to its simplicity and low costs, the sol–gel method is the most popular. However, it is obvious

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http://dx.doi.org/10.1016/j.ceramint.2012.09.046

that the properties of the film, and consequently its applications, will strongly depend on the nature of the preparation process as well as on its operational parameters.

Although, thanks to its simplicity, the sol–gel process is often used to synthesize TiO_2 films for photocatalytic application, it needs relatively high temperatures, ranging up to 500 °C [3,16–18]. On the other hand, the PECVD method, which requires much lower temperatures and allows one to deposit coatings onto temperature-sensitive substrates, is not very frequently used for that purpose. In our previous papers, we described amorphous coatings, obtained with the PECVD technique, which exhibited both strong bactericidal activity and considerable superhydrophilic effect on their exposure to UV light [22–24]. Unfortunately, a comparison of these results with those obtained by other workers is very difficult, if not impossible, mainly due to a deficiency of standard conditions of irradiation (power of radiation, distance from the sample, radiation spectrum, time of illumination, air temperature and humidity). Therefore, the aim of the present work is to compare the photocatalytic properties, studied under identical conditions, of amorphous TiO_2 films prepared with the PECVD technique with those exhibited by amorphous and crystalline coatings synthesized with the sol–gel method. In addition, all the coatings have been characterized with respect to their morphology as well as their chemical and phase composition.

2. Materials and methods

2.1. Film preparation

In order to study their photocatalytic and other utility properties, titanium oxide coatings were always deposited, in both methods of synthesis, on glass substrates. These were microscopic borosilicate glass slides of the hydrolytic class 1 and dimensions $7 \times 20 \times 0.1$ mm^3. Other substrates, namely silicon wafers of (111) orientation and dimensions $7 \times 20 \times 1.5$ mm^3, were used for the purpose of sample preparation for thin film diagnostics with the AFM, FTIR and XRD analytical techniques.

In the sol–gel process, titanium (IV) butoxide of 97% purity, manufactured by Aldrich, was used as the titanium precursor. Titania sol was prepared from that compound by mixing it with absolute ethanol, acetic acid and distilled water at room temperature. The coatings were deposited using the dip-coating method by withdrawing the substrate from the sol at a constant rate of 0.8 mm/s. In the subsequent steps, samples were dried in ambient conditions for 15 min and thermally annealed for 15 min at a temperature of either 300 °C or 500 °C.

For the RF PECVD synthesized films, vapors of titanium tetrachloride (Aldrich, purity 99.0%) diluted in argon and mixed with oxygen were used as the starting material, while the depositions were performed in a parallel plate reactor. In this reactor, the lower, sample holding, electrode was powered by an RF field, as described in Refs. [23,24]. The flow rates of oxygen and argon were empirically selected to be 40 sccm and 2 sccm, respectively, and the working pressure amounted to 0.4 Torr. The flow rate of $TiCl_4$ vapors was regulated by adjusting the temperature of the liquid, with the optimum value of that temperature being 0 °C. The RF power of glow discharge varied in a range between 100 W and 300 W and the deposition time equaled 45 min.

2.2. Characterization of the films

Morphology of the films on glass substrates was studied using a Hitachi S-3000N scanning electron microscope (SEM), while their elemental composition was followed with a Noran X-ray energy dispersive spectroscopy detector (EDS), coupled with the microscope. The thickness of the coatings was measured with a Hommel Tester T1000 profilometer equipped with a Waveline-20 detector. Surface topography of the TiO_2 coatings, deposited on silicon substrates, was investigated with a Nanoscope IIIa Multi-Mode, Digital Instruments, atomic force microscope (AFM), the images being recorded with a resolution of 512×512 lines.

X-ray diffraction (XRD) was used to identify the coatings crystalline structure. The films obtained by the sol–gel method were analyzed with a step scan Siemens D-500 X-ray diffractometer. Co K_α characteristic radiation and a graphite monochromator were employed for the analysis. A step technique was used in these measurements, with each step amounting to 0.05° and a counting time of 3 s. Identification of phase composition was carried out with the help of X-RAYAN computer software, supported by the International Centre for Diffraction Data (ICDD) database. Diffraction spectra were analyzed in the intensity-2θ angle coordinates. XRD patterns of the films obtained with the PECVD method were recorded with a Siemens 5000 X-ray diffractometer using Cu K_α radiation with the LiF monochromator in the detector arm. Classical Bragg–Brentano geometry was used for the measurements. The measurements were carried out at the constant angle of incidence of 0.5°. The reflected radiation was recorded in the 2θ range between 16° and 65° with steps of 0.05° and a counting time of 50 s.

Chemical bonding of the coatings was analyzed by means of Fourier Transform Infrared Spectroscopy (FTIR) using an ATI Mattson model Infinity AR 60 spectrometer in the spectral range of 4000 cm^{-1}–500 cm^{-1}.

Photocatalytic activity of the films prepared by both methods was evaluated with respect to their bactericidal properties. An exponentially grown phase of *Escherichia coli* strain DH5-alpha was used as a model microorganism. Cultures were grown in the Luria–Bertani medium, containing 1% NaCl, 1% peptone G, and 0.5% yeast extract under aerobic conditions. The growth was continued until the number of cells reached 106 cells/ml. Suspensions of *E. coli* cells were pipetted onto TiO_2 coated glass plates and spread out to form a liquid film. The illuminating UV

light source was placed 20 cm above the sample surface. Light intensity was 16 mW/cm^2 and an irradiation time of up to 2 min was used. The results of the treatment were observed using an Olympus GX 71 optical microscope equipped with a digital camera, model DP70. The numbers of killed and surviving bacterial cells were determined for each coating, and the uncoated glass was used as a reference. The results were evaluated using bactericidal activity, defined as the percentage of bacterial inhibition:

$$BI = \left[(C_t - C_s)/C_t\right] \times 100\%$$

where C_t denotes the total number of bacteria being irradiated and C_s denotes the number of bacteria that survived [25].

Water contact angle measurements for both kinds of coatings deposited on glass substrates were performed using a Krüss Easy Drop contact angle system. Each measurement was performed after the sample had been stored in the dark for at least 48 h. The sample was mounted on the system table, then a 30 μl droplet of deionized water was placed on its surface and contact angle measurement was taken instantly. After the first measurement, the samples were irradiated for 110 min at a distance of 20 cm with a Polam ZWLE-ZPL mercury lamp, working in the wavelength range of 320–400 nm, and contact angle measurements were taken again. The measurements were performed at a temperature of 22 °C with a relative humidity of 40%.

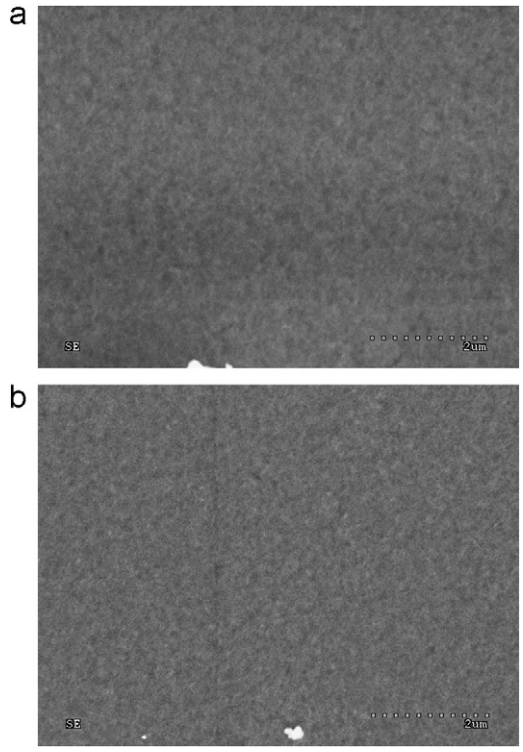

Fig. 1. SEM images of TiO_2 films deposited by the sol–gel method, annealed at (a) 300 °C and (b) 500 °C.

3. Results and discussion

3.1. Surface morphology and chemical composition

SEM images of the surface of the coatings synthesized with the sol–gel method are presented in Fig. 1. As seen in the figure, the investigated films are smooth, continuous, and pinhole-free, with no cracks and no visible effect of the heat treatment.

The images of the films deposited using the RF PECVD method, at the different glow discharge power input values of 100 W, 200 W, and 300 W, are shown in Fig. 2. All films were continuous, but for the power magnitude exceeding 100 W a number of aggregates were observed on the surface with their quantity increasing with power.

The elemental composition of both type of films was evaluated by EDS. It was found that the sol–gel coatings consist exclusively of titanium and oxygen, but films obtained by the RF PECVD method also include approximately 5–7% of Cl. The chlorine content increases with the power of discharge, which is a likely result of an increasing quantity and activity of monomer originated chlorine and its secondary incorporation into the growing film. The atomic ratio O/Ti changes from 1.5 for 100 W to 2.0 for 300 W of discharge power.

The thickness of the films prepared using the sol–gel method amounted to 120 nm and 80 nm respectively for films annealed at 300 °C and 500 °C. RF PECVD film thicknesses were evaluated to be 85 nm, 150 nm and 525 nm respectively for 100 W, 200 W and 300 W of the discharge power of deposition.

The AFM images of the surface of the coating synthesized using the sol–gel method and thermally annealed at 500 °C are presented in Fig. 3 while those of the films deposited using the RF PECVD technique at 200 W and 300 W are shown in Fig. 4. In all the presented cases silicon wafers were used as substrates. As seen in the figures, the surface is not always smooth. Granulate structures are observed in certain cases and these structures appear to have sharper edges in the case of sol–gel produced coatings, which may result from the presence of a crystalline phase. Distribution of the spheres is uniform and their dimensions remain in the range of 20–30 nm. As far as the RF PECVD synthesized films are concerned, they exhibit uniformly distributed granules for the discharge power of 200 W. Increase of the power, however, results in the agglomeration of these structures. The dimensions of the majority of granules remain in the 10–20 nm range. An analysis of the images allowed us to assess the surface roughness R_a as well as the Root Mean Square (RMS). Both parameters are substantially higher in the case of the films deposited using the RF PECVD method and they increase with the increasing discharge power. While being $R_a = 5.1$ nm, RMS = 6.4 nm for the discharge power of 200 W they increase to $R_a = 6.6$ nm and RMS = 11.8 nm for the power of 300 W. The respective values for the sol–gel synthesized coatings are much smaller: $R_a = 0.3$ nm and

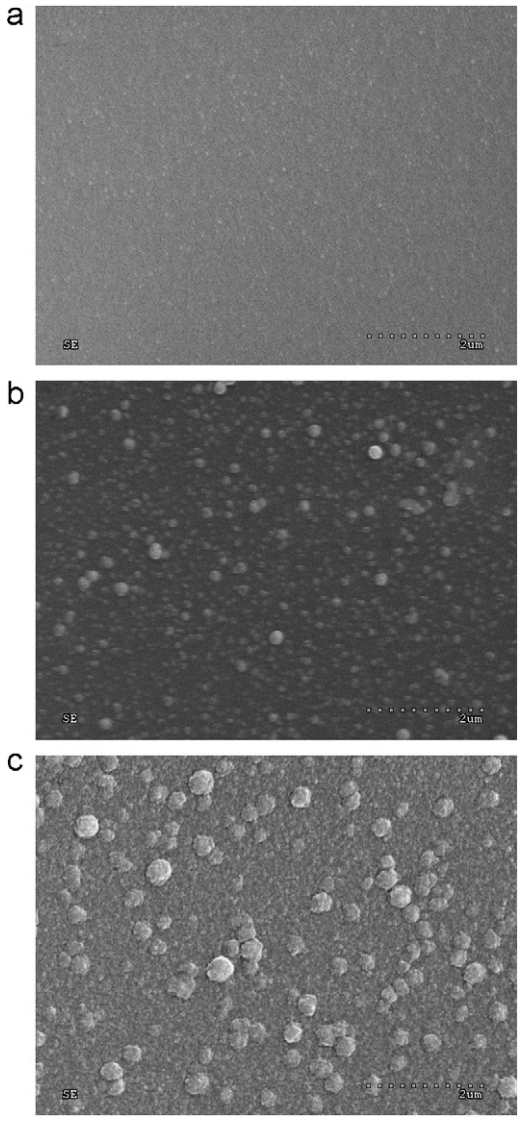

Fig. 2. SEM images of the TiO_2 films deposited by RF PECVD with the glow discharge power of (a) 100 W, (b) 200 W, and (c) 300 W.

RMS=2.1 nm. Such differences between both types of materials may be partly due to different thicknesses of the respective coatings.

3.2. Structure of the films

The crystalline structure of the films was analyzed using the XRD method. Diffraction patterns of all the investigated films are shown in Fig. 5. The crystalline structure of the sol–gel films depend on annealing temperature. With the application of the Co K_α radiation line, the diffraction signals for anatase should appear at 2θ values of 29.44 (101); 44.19 (004); 56.42 (200); 63.5 (105); 64.92 (211); and 74.32 (204)—according to the 21-1272 ICDD card, while those for rutile should appear at 2θ values of 32.00 (110); 42.18 (101); 48.28 (111); 64.06 (211) 66.90 (220); and 82.32 (301) according to the 21-1276 ICDD card. None of the above listed signals appeared in the diffractograms of the sol–gel films annealed at 300 °C (see Fig. 5a)—these materials are shown to be clearly amorphous. However, when thermal annealing is carried out at a temperature of 500 °C, the anatase structure appears in the coating, with the presented maxima well corresponding to all the 2θ values characteristic for this polymorph.

As far as the PECVD deposited titanium oxide is concerned, for which the Cu K_α radiation line was used in the experiment, no signals characteristic for any crystalline structure of TiO_2 were observed independent of the deposition conditions (see Fig. 5b). For anatase, these signals should be observed at 2θ values of 25.28 (101); 37.8 (004); 48.04 (200); 53.89 (105); 55.06 (211); and 62,69 (204) (ICDD card: 21-1272), while for rutile at 2θ values of 27.47 (110); 36.12 (101); 41.26 (111); 54.37 (211); 56.69 (220); and 69.07 (301) (ICDD card: 21-1276). The single diffraction peak in the recorded pattern (2θ=28.5) is not characteristic for any crystalline form of titanium oxide and it corresponds to the (111) plane of the silicon substrate

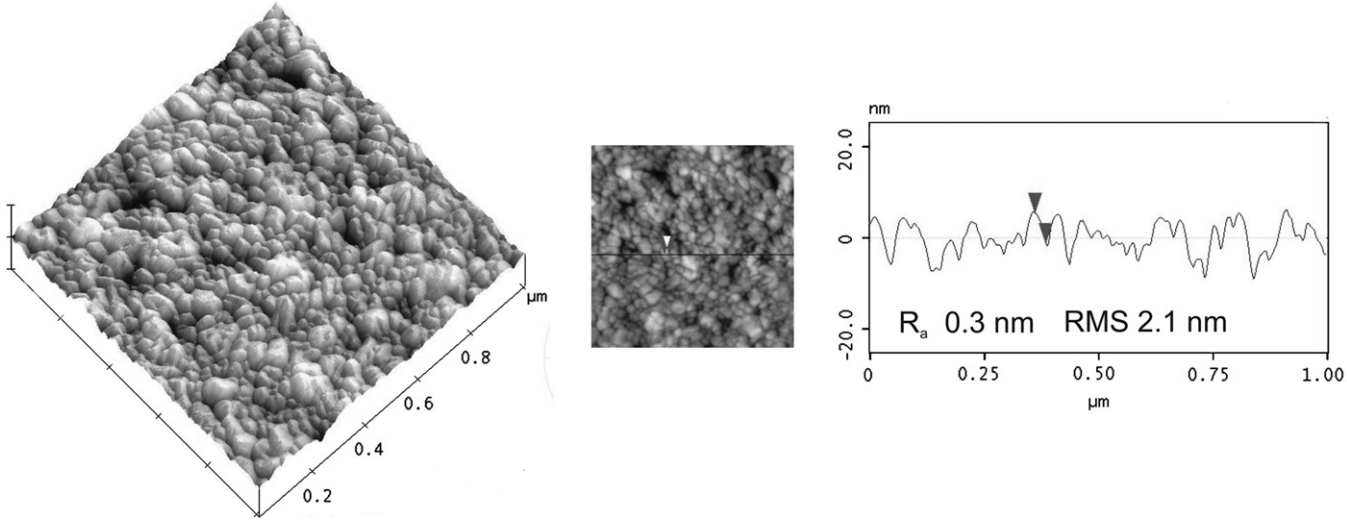

Fig. 3. AFM micrograph of film deposited using the sol–gel method and annealed at 500 °C.

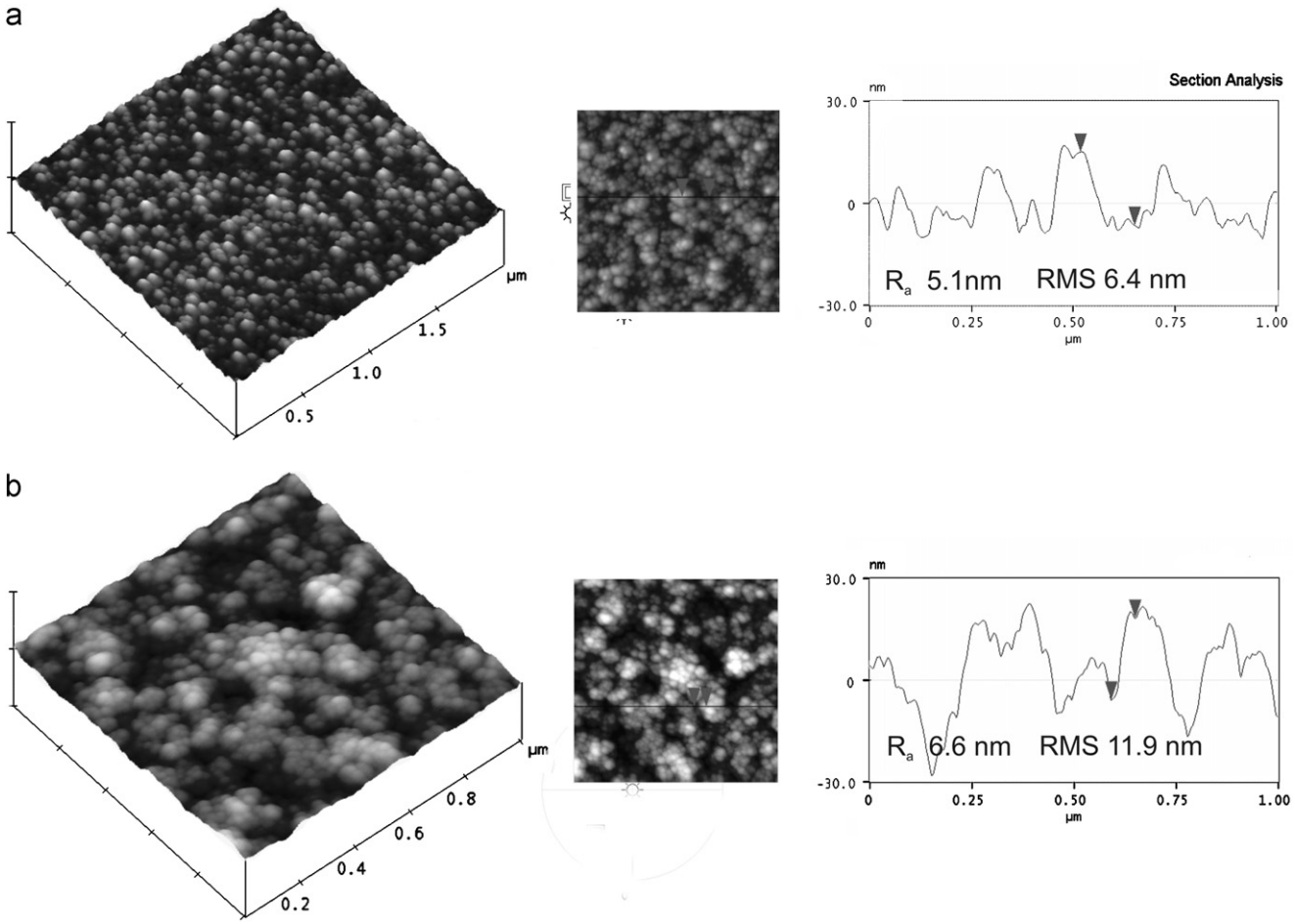

Fig. 4. AFM micrographs of films deposited using the RF PECVD method with the glow discharge power of (a) 200 W and (b) 300 W.

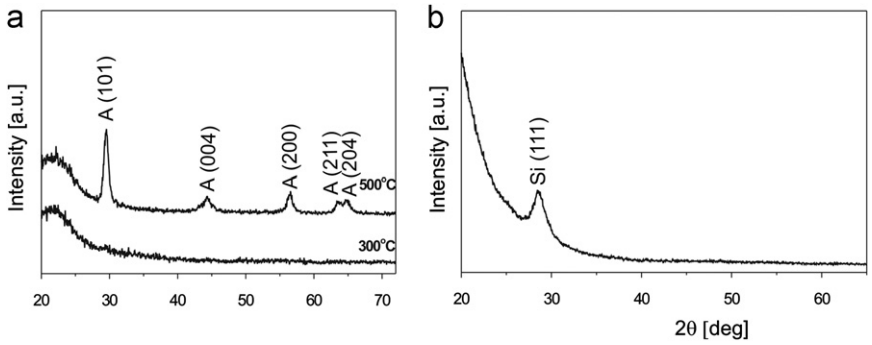

Fig. 5. XRD patterns of titanium oxide films deposited by (a) sol–gel method, annealed at 300 °C and 500 °C, using Co K_α radiation and (b) RF PECVD method, 300 W, using Cu K_α radiation.

(ICDD card: 27-1402). The results of X-ray diffraction fully confirm the amorphous character of the RF PECVD synthesized titanium dioxide coatings, already reported by some of us in Ref. [24], with the only difference being the number and the intensity of the substrate related diffraction lines.

Fig. 6 shows FTIR spectra of both types of films, obtained at different parameters of deposition. The principle differences between the spectra are found in the 1100–500 cm^{-1} range, corresponding to the absorption of titanium–oxygen bonds. The band at 785 cm^{-1} is due to the absorption of the Ti═O group (suboxide), while that at 500 cm^{-1} is connected with the absorption of Ti–O bonds in a configuration where every Ti atom is bound to four atoms of oxygen (dioxide). For films deposited using the RF PECVD method (see Fig. 6b), the 785 cm^{-1} band is considerably stronger for the sample obtained with the power of 200 W than for the sample obtained at 300 W,

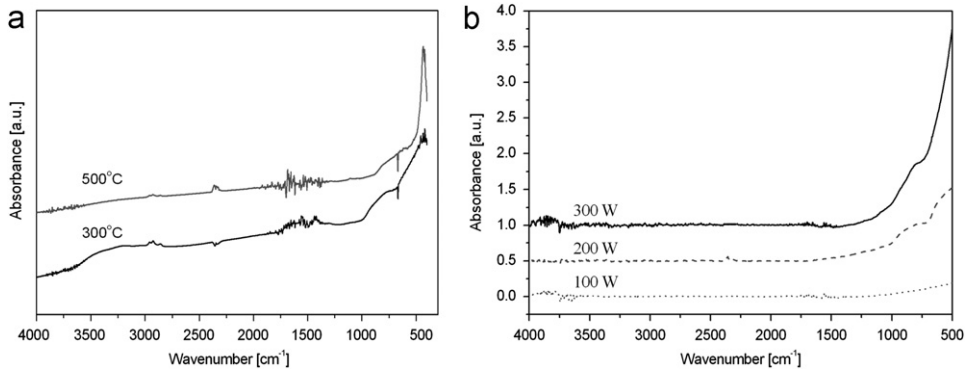

Fig. 6. FTIR spectra of titanium oxide films deposited by (a) sol–gel method annealed at 300 °C and 500 °C and (b) RF PECVD method at 100 W, 200 W and 300 W of discharge power.

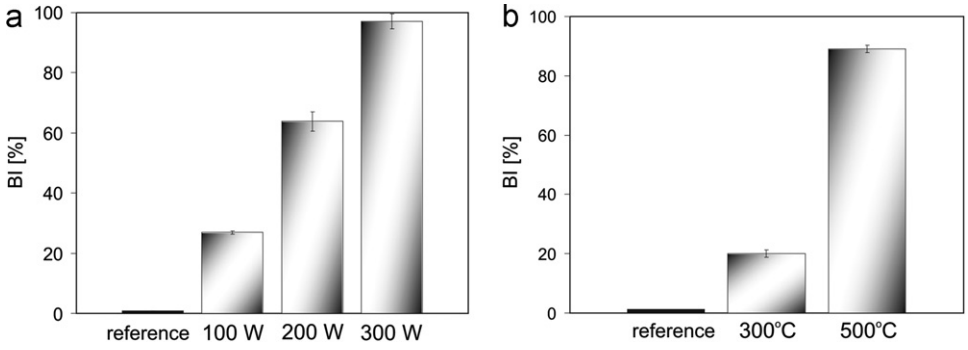

Fig. 7. Bactericidal effect BI of titanium oxide films deposited on glass by (a) sol–gel method heat-treated at different temperatures and (b) RF PECVD method at different RF power inputs.

and it is completely absent in the 100 W sample. The intensity of the 500 cm^{-1} band is greatest in the film synthesized at 300 W, and lowest for the film deposited at 100 W. A similar effect is observed for the sol–gel thin films presented in Fig. 6a. The 500 cm^{-1} maximum is more intensive for the coatings treated at 500 °C than for those annealed at 300 °C. The sol–gel coatings are characterized by additional absorption bands in the vicinity of 3000 cm^{-1}. These are due to the vibrations of carbon–hydrogen bonds in the following groups: $–CH_3$ (2962 cm^{-1}), $–CH_2$ (2926 cm^{-1}) and –CH (2890 cm^{-1}). These bands constitute a representation of the presence of methyl groups from the unreacted organic precursor, which is additionally confirmed by the absorption bands in the range 1400–1600 cm^{-1}. The absorption intensity decreases after thermal annealing, which is a likely result of the removal of carbon from the coating material. Absorption spectra of the RF PECVD samples obtained at the power magnitudes of 100 and 300 W as well as those of the films deposited using the sol–gel technique show considerable bands of absorption at 3500–4000 cm^{-1} and at about 1600 cm^{-1}, connected with the absorption of the –OH group. Because the formation of water from the precursors used in the deposition processes is impossible, the above results strongly suggest that adsorption of water takes place on the layer after its exposure to the atmosphere. These bands are the most intensive in the case of the film annealed at 300 °C.

3.3. Photocatalytic activity and hydrophilicity

Photocatalytic activity of titanium oxide films synthesized in this work was evaluated by bactericidal tests. The percentage of bactericidal inhibition BI for the examined coatings is presented in Fig. 7.

Under steady experimental conditions, UV irradiation alone caused the death of 2% of the population of bacteria on the uncoated glass and this value was used as the test reference. Titanium oxide coated surfaces revealed much higher BI values under the same conditions of irradiation. The rate of bacterial death increased with the annealing temperature for sol–gel coatings and with the power of RF input for RF PECVD deposited films. The sol–gel titania coating treated at 300 °C after UV irradiation killed about 20% of population of bacteria, but for the coating annealed at 500 °C the BI index amounted to 90% (Fig. 7a). The bactericidal properties of sol–gel coatings are strongly connected to their structure; films annealed at 300 °C are amorphous but those annealed at 500 °C revealed the crystalline structure of anatase. In the case of RF PECVD titanium oxide coatings the BI index increased from 25% for 100 W of RF input power to 98% for 300 W (see Fig. 7b). This is an interesting finding, especially in view of the fact that TiO_2 films synthesized at the glow discharge power of 300 W are stoichiometric, but amorphous at the same time.

Table 1
Dependence of water contact angle for titanium oxide film prepared by RF PECVD and sol–gel methods on RF power input and the temperature of annealing, respectively.

Type of film	Temperature/power	Before UV irradiation [deg.]	After UV irradiation [deg.]	Reduction [deg.]
Sol–gel	300 °C	67.8	42.5	25.3
	500 °C	45.7	11.7	34.0
RF PECVD	100 W	92.5	66.8	25.7
	200 W	91.8	54.8	37.0
	300 W	95.6	41.7	53.9

Photo-induced hydrophilicity was evaluated using the water contact angle measurements. Results of these measurements are presented in Table 1.

The values of water contact angle of the sol–gel coatings strongly depend on their heat-treatment temperature and consequently on the structure of the film. The initial value of the contact angle for the samples thermally annealed at 300 °C points to the hydrophilic character of their surfaces, and annealing at 500 °C leads to a further rise of their hydrophilicity through an increase of the content of surface polar moieties. The change of the water contact angle of the amorphous (300 °C) coating, annealed at the lower temperature, following its illumination with UV light was not large and amounted to 25° In the case of the crystalline coating, annealed at 500 °C, after illumination the water contact angle dropped to 11.7°, which places it near superhydrophilic materials. As far as the RF PECVD synthesized titanium oxide films are concerned, before UV irradiation the values of water contact angle were all higher than 90° and they were rather independent of the power of glow discharge. This suggests an advantage of dispersive interactions over polar ones, thus making the surface hydrophobic. After irradiation, the samples showed a more hydrophilic character, and the water contact angle decreased with an increase of RF power of their deposition. The hydrophilic effect was strongest in the case of films deposited at 300 W, where the contact angle following irradiation was equal to 41.7° Although this value is similar to that of the amorphous sol–gel coating and lower than that of the crystalline film, the contact angle reduction is the highest in this case.

4. Conclusions

In this work, photocatalytic TiO_2 coatings were prepared on glass and silicon substrates using two different methods: sol–gel and RF PECVD techniques. Morphology, structure and photocatalytic activity of the films were compared.

It has been found that the structure of sol–gel coatings depends on the annealing temperature: following heat treatment at 300 °C the TiO_2 films were amorphous, while after annealing at 500 °C they became crystalline (anatase). RF PECVD deposited films, on the other hand, were amorphous in the entire range of RF power input of 100–300 W. The FTIR measurements show that the best TiO_2 stoichiometry of the RF PECVD films was achieved in the case of materials deposited at 300 W, while for the sol–gel layers thermal annealing at 500 °C assured the optimum composition. The results obtained show a substantial enhancement of bactericidal activity of UV radiation for both kinds of investigated films. Among all the materials, the films deposited at 300 W of RF input power by the RF PECVD method and those annealed at 500 °C in the sol–gel technique exhibited the highest bactericidal effects, amounting to over 90% of bacteria killed. In spite of their amorphous character the RF PECVD deposited films showed even higher rates of bactericidal activity than those prepared with the sol–gel technique. One of the reasons for these differences may be connected with the surface topography of the films. The roughness of the RF PECVD materials is much higher, which substantially increases the area of surface contact of the bacterial culture with the coating. Although the highest reduction of water contact angle after UV irradiation was found in the case of anatase films synthesized using the sol–gel technique (and annealed at 500 °C), it is justified to say that both types of titanium oxide films exhibited a strong photo-induced hydrophilic effect.

It has been proved that it is possible to produce good quality photocatalytic titanium oxide films using both sol–gel and RF PECVD techniques. This conclusion is particularly important in relation to the RF PECVD method as it makes possible deposition of TiO_2 coatings on temperature-sensitive substrates.

Acknowledgments

The work has been supported by the Ministry of Science and Higher Education within the frame of the Grant no. N 508 48 26 38.

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