BACTERICIDAL AND HYDROPHILIC PLASMA DEPOSITED THIN TiO₂ FILMS ON GLASS SUBSTRATE

Anna Sobczyk-Guzenda[1*], Hieronim Szymanowski[1],
Maciej Gazicki-Lipman[1], Jacek Kowalski[1],
Witold Jakubowski[1], Tomasz Halamus[2]

[1] Institute of Materials Science and Engineering,
Technical University of Lodz,
1 Stefanowskiego Str., 90-924 Łódź, Poland
[2] Chair of Molecular Physics,
Technical University of Lodz,
116 Żeromskiego Str., 90-924 Łódź, Poland
* e-mail: asobczyk@p.lodz.pl

Abstract

In recent years, titanium dioxide has attracted a great deal of attention as a material for photocatalytic applications. These applications include anti-bacterial effect as well as photocatalytic air and water purification. Another property of TiO₂ concerns a substantial increase of its surface hydrophilicity upon irradiation. The aim of this work is to investigate thin TiO₂ films obtained by RF PECVD technique with respect to hydrophilic and long-term bactericidal activity. Structural studies, carried out by Raman spectroscopy show that all the investigated coatings are amorphous. The films exhibit agglomerates, with their amount depending on energetic conditions of deposition. Adhesion measured by a scratch test shows that films deposited at higher RF power adhere better than those synthesized at lower power values. UV irradiation causes death of nearly 100% of Escherichia coli population on TiO₂ films. The irradiated films are still active for about 30 min after the end of UV exposure. A substantial decrease of water contact angle is also observed upon the irradiation of the films with UV light.

Keywords: TiO₂ thin films, RF PECVD method, bactericidal activity, hydrophilic effect

Introduction

Titanium dioxide (TiO_2) is a chemically stable and harmless material, and it is widely applied in various fields. For example, it is used for optical and protective coatings, photo-electrodes, high-k dielectrics, paints, cosmetics, etc. [1,2,3]. It is also very attractive as a biocompatible coating on medical implants, where a protective surface layer of TiO_2 considerably increases the wear resistance and hardness [4].

Titanium dioxide exhibits photoinduced phenomena. All the photoinduced processes originate from the semiconductor band gap. When a photon with energy higher than this band gap strikes the material, it gets absorbed and an electron is promoted to the conductive band, leaving a hole in the valance band. This excited electron can either be used directly to create electricity in a photovoltaic cell or can drive a chemical reaction by the virtue of photocatalysis [1,2,5,6]. Titanium dioxide has been broadly investigated as a semiconducting photocatalyst for its application in solar energy conversion and environmental purification since Fujishima and Honda [7] discovered the photocatalytic splitting of water on TiO_2 electrodes in 1972. Another interesting phenomenon, termed 'photoinduced superhydrophilicity' (PSH), was recently discovered by Wang et al. [8]. This phenomenon is connected to the fact that trapping holes at the TiO_2 surface causes a high wettability and that surface. Highly hydrophilic surfaces have many practical applications, for example in a manufacture of self-cleaning and antifogging materials. All the photoinduced phenomena involve surface bound redox reactions [1,8]. By far, the most active field of TiO_2 photocatalysis is the photodegeneration of organic compounds [6,9,10]. TiO_2 has become a photocatalyst in environmental decontamination for a large variety of organics, viruses, bacteria, fungi, algae, and cancer cells, which can be totally degraded and mineralized to CO_2, H_2O, and harmless inorganic anions. Many reports concerning bactericidal effects of TiO_2 appear and they often refer to hydroxyl radicals OH· being the toxic agent [1]. Dorfman and Adams (1973) [11] state that OH· reacts with most biological molecules at diffusion controlled rates. For that reason an inactivation of *Escherichia coli* by hydroxyl radicals that are generated by photocaltic action depends upon both mass transfer limitations through the cell wall or cell membrane and the short half life of a radical [12]. Matsunaga et al. (1988) [13] suggests that hole in the valence band receives an electron from a coensyme-A (CoA) as the donor formic dimeric CoA. Dimerisation of CoA inhibits respiration and causes death of the cells. The TiO_2 photocatalytic disinfection approach offers a number of positive features: 1) the oxidant is the atmospheric oxygen, 2) the catalyst of TiO_2 is nonhazardous, inexpensive and rugged, inert for human and environmental, 3) the oxidation process is powerful and indiscriminate with the potential of causing death in most types of microorganism. Photoinduced bactericidal activity of titanium oxide can lead to different applications, including disinfections in diverse environments. In the ceramic and construction industry, the photoinduced bactericidal effect of titanium oxide can be of special interest. This is particularly true when a ceramic material is placed in microbiologically sensitive environments, such as medical facilities, production or experimental environments, where biological contamination must be prevented [14].

Films of TiO_2 can be synthesized by a number of high temperature deposition techniques including sol-gel [1,15], metalorganic chemical vapour deposition (MOCVD) [16], reactive magnetron sputtering [17], spray pyrolysis [18], and hydrothermal method [19]. Plasma enhanced CVD (PECVD) has many advantages such as low deposition temperature, high purity, good step coverage, and easy control of reaction parameters [20]. However, there are very few reports in which the PECVD technique for the preparation of TiO_2 films as a photocatalyst [21,22].

Titanium dioxide crystallizes in three modifications: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Rutile is the most stable phase yielded by most crystal growth processes. Anatase is less dense and less stable than rutile. Nevertheless, at comparatively low temperatures (< 600-800°C) anatase can be stabilized in the form of powder, thin films, ceramics, and synthetic or natural crystals. Both crystal structures, anatase and rutile, are commonly used as photocatalyst with anatase showing greater photocatalytic activity in most reactions [1,2]. It is usually reported that amorphous structure does not show photocatalytic properties [1,2,9,10], but there are few reports in the literature concerning super hydrophilic effect recorded for amorphous TiO_2 surfaces [23,24].

In the present work, thin films of titanium oxide, designed for photocatalytic applications, were deposited by means of radio frequency (RF) PECVD technique. The purpose of the work was to obtain homogenous amorphous films showing good bactericidal activity and substantial water wettability.

Materials and methods

The titanium oxide films were deposited on glass substrates in a RF PECVD reactor. The chamber of this reactor consists of two parallel electrodes with a glass cylinder separating them. The upper electrode is a grounded, shower-type electrode, through which a stream of titanium tetrachloride vapor, diluted in argon, is introduced to the chamber. The second reactive gas (oxygen) is also introduced to the chamber in the same way. The lower electrode is supplied with RF power from the Plasma Products RF5S power generator through a self–made matching circuit. MKS 1179AX mass flow controllers are used to control the flow rates of gaseous media (argon and oxygen). The flow rate of titanium tetrachloride was regulated by the temperature of liquid precursor and by flow rate of argon. The optimum value of liquid $TiCl_4$ temperature was found to be 0^oC. The deposition time was 45 min. The power of deposition was 100, 200 and 300 W.

The structure of the films was analyzed by means of Raman Shift Spectroscopy (RSS). The Raman analysis was performed using the dispersive spectrometer Jobin-Yvon T64000 equipped with a confocal microscope. The spectra were obtained at the temperature of 293 K using the argon ion laser wavelength $\lambda = 514.5$ nm. All the measurements were conducted twice, first time for as-deposited samples and second time after the samples had been annealed at 450^oC for 1 h.

The morphology of titanium dioxide surfaces was observed with the help of scanning electron microscope (SEM), Hitachi, model S-3000N.

Adhesion was made by scratch test using a self-made equipment. High loads were obtained in one scratch with load increasing from 1 N to 10 N with 1 N steps.

For testing bactericidal activity of the coatings, an exponential growth phase of *Escherichia coli* strain K12 was used as a model microorganism. Cultures were grown aerobically in Luria-Bertani (LB) medium, containing 1% of NaCl, 1% of peptone G, and 0.5% of yeast extract. The growth was continued at least until the number of cells reached a 10^6 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 (Polam ZWLE-ZPL mercury lamp) was placed 200 mm above the sample surface. Light intensity was 16 mW/cm^2 and an irradiation time of up to 2 minutes was used. The results of the treatment were observed with the help of an Olympus GX 71 optical microscope, equipped with a digital camera, model DP70.

The numbers of killed and surviving bacteria cells were determined for each coating at different power of deposition, and uncoated glass was used as reference. Long-term bactericidal activity was measured for 60 min with 15 min step. The results were evaluated using bactericidal activity, defined as the percentage of bacterial inhibition BI.

Contact angle measurements were performed with the help of camera and self-made software. The measurements were carried out after the samples had been stored in dark for at least 48h. Each sample was mounted on the table of the measurement system and a 30 µl droplet of deionized water was placed on its surface. Contact angle measurement was taken immediately. After the first measurement, the sample was irradiated for the time of 110 minutes at a distance of 20 cm with a UV lamp, and contact angle measurements were taken once again. The wettability of a surface was characterized in terms of the surface free energy. For that purpose, the Owens model [25] was applied, in which surface energy is divided into a dispersion component γ^d and a polar component γ^p. The dispersion components is mainly due to the hydrophobic moieties, e.g. methyl groups. The polar component originates mainly from polar moieties, e.g. hydroxyl and carbonyl groups. The surface free energy was obtained by measuring contact angles of two liquids of significantly different polarities, with the defined dispersive and polar components, namely methylene iodide and water.

Results and Discussions

The morphology of the films deposited with the help of RF PECVD method at the power of 100 W, 200 W, and 300 W is shown in FIG. 1. The titanium dioxide films are not nanoscopically smooth but appear to be formed of tiny granules forming larger aggregates. All films were continuous but for the power of glow discharge higher than 100 W a number and size of globules were observed on the surface and their quantity increased with the power of deposition. This is a particularly advantageous phenomenon because a development of the surface area substantially increases the overall photocatalytic effect.

Two samples have been subjected to Raman spectroscopic analysis: one deposited at the power of 200 W and the other produced at the power of 300 W. Since the ultimate subject of analysis was a presence of crystalline forms of titanium dioxide, the 100 Watt sample, presumably containing very little of that oxide, was not analyzed. In the spectrum of plain silicon the following wavebands have been assigned as being characteristic for silicon: 129 cm^{-1}, 143 cm^{-1}, 173 cm^{-1}, 222 cm^{-1}, 268 cm^{-1}, 303 cm^{-1} and 435 cm^{-1}. In addition, the wavebands at 122.5 cm^{-1} and at 160 cm^{-1} have been identified as laser plasma lines.
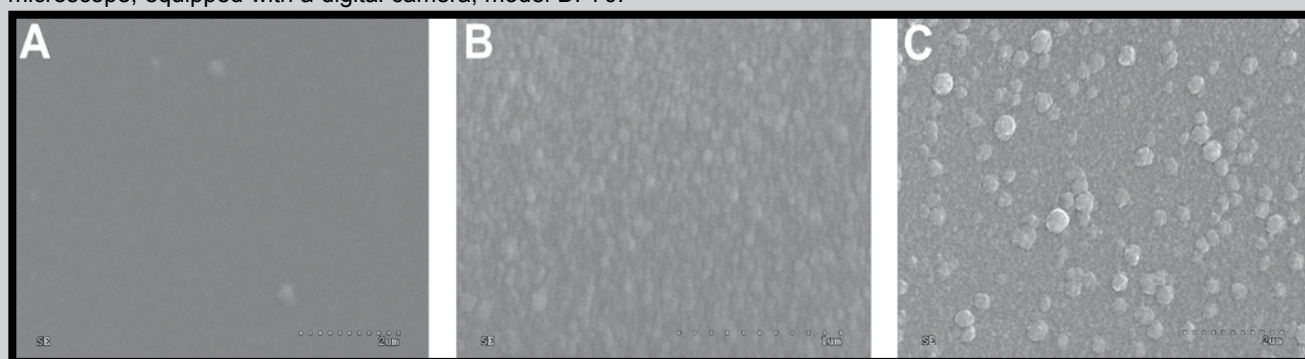

FIG. 1. SEM micrographs of TiO$_2$ films deposited by RF PECVD technique at the power of: A – 100 W, B – 200 W, C – 300 W.
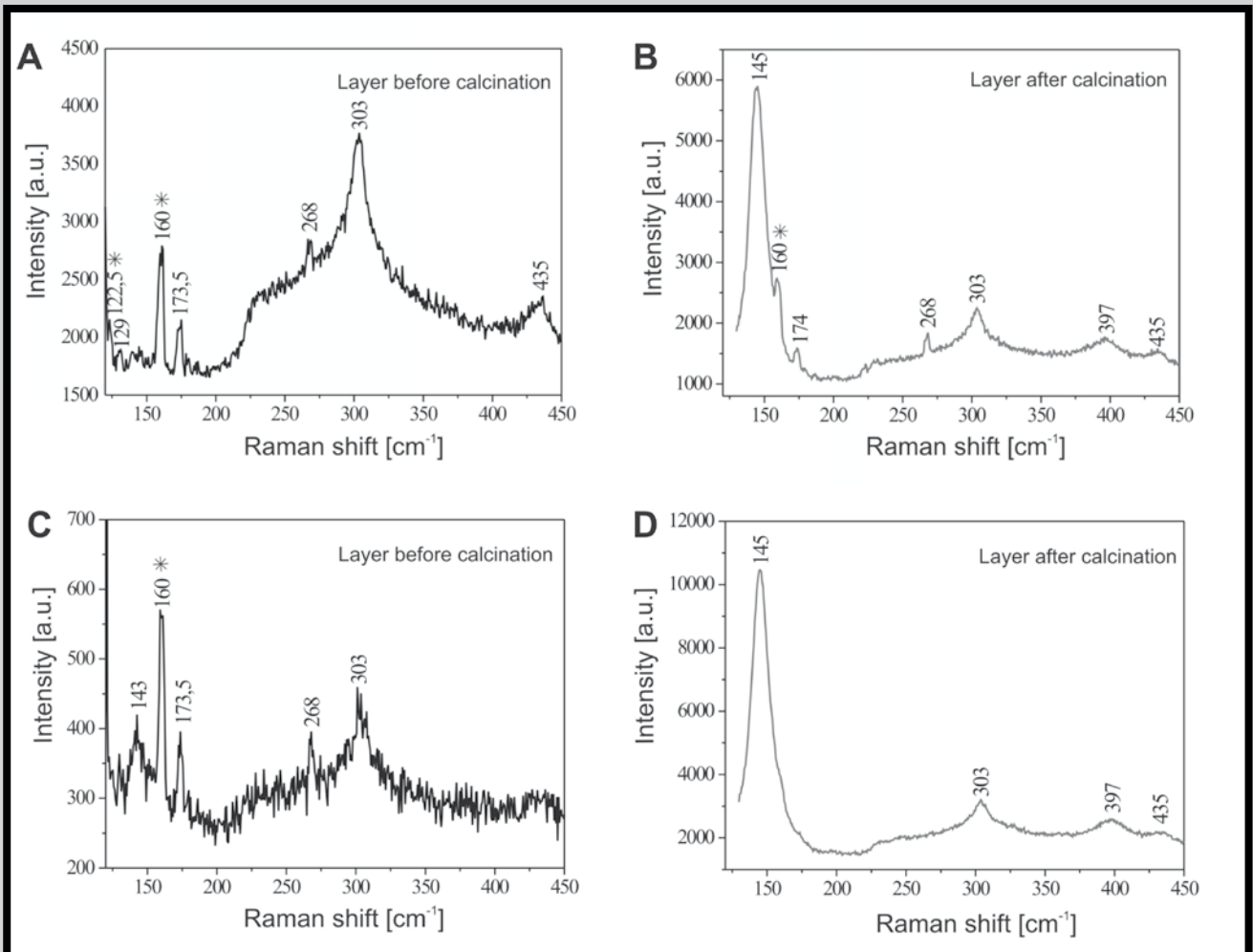
FIG. 2. Raman spectra of thin titanium oxide films: deposited at 200 W without annealing (A), following thermal annealing at 450°C for 1 hour (B), deposited at 300 W without annealing (C) and following thermal annealing at 450°C for 1 hour (D).

As far as the crystalline forms of titanium dioxide are concerned, according to the theory of groups, three kinds of active Roman modes $A_{1g}+2B_{1g}+3E_g$ should occur in the spectrum of anatase. For a single crystal of this form, Ohsaka [26] has distinguished the following wavebands: 144 cm^{-1} (E_g), 198 cm^{-1} (E_g), 400 cm^{-1} (B_{1g}), 515 cm^{-1} ($B_{1g}+A_{1g}$), 640 cm^{-1} (E_g). In the case of rutile, there exist four active Raman modes: $A_{1g}+B_{1g}+B_{2g}+E_g$ and the following wavebands have been assigned in the spectrum of rutile single crystal: 143 cm^{-1} (B_{1g}), 447 cm^{-1} (E_g), 612 cm^{-1} (A_{1g}), 826 cm^{-1} (B_{2g}) [27].

The spectra of the as-deposited layers produced at 200 W and 300 W of RF power are presented in FIG. 2A and 2C, respectively. As seen in the figures, none of the above listed wavebands, distinctive for any of the crystalline forms of TiO$_2$, are present in these spectra. Their absence clearly demonstrates an amorphous nature of the as-deposited coatings. These spectra differ from each other only with regard to the quantity and intensity of peaks originating from the substrate.

In order to confirm the amorphous nature of the investigated films, their thermal annealing was performed for 1 hour at 450°C. As seen in FIG. 2B and 2D, following this procedure the wavebands typical for the anatase appear in both spectra at wavenumbers 145 cm^{-1} and 397 cm^{-1}. In FIG. 2D, the peaks characteristic for crystalline phase of anatase show their highest intensity, which reveals a presence of the largest quantity of amorphous stoichiometric TiO$_2$ in the as-deposited layer. In both cases, apart from the wavebands
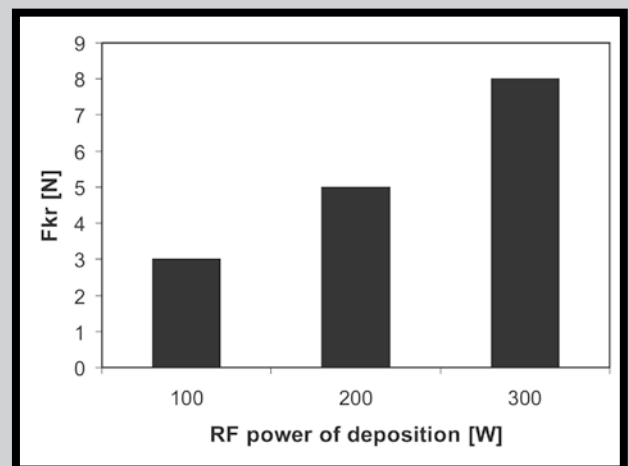

FIG. 3. Changes of critical adherence force for samples deposited at different RF power.

distinctive for anatase, there are also peaks originating from the silicon substrate appearing in the spectra. Using the confinement model [28,29], from the position of the anatase main Raman peak it is possible to obtain a rough estimation of a crystal size. In the case of titanium dioxide films deposited at the RF power of 200 W and 300 W the main band for anatase is centered at 145 cm^{-1}, which corresponds to a crystal size of approximately 15-20 nm.
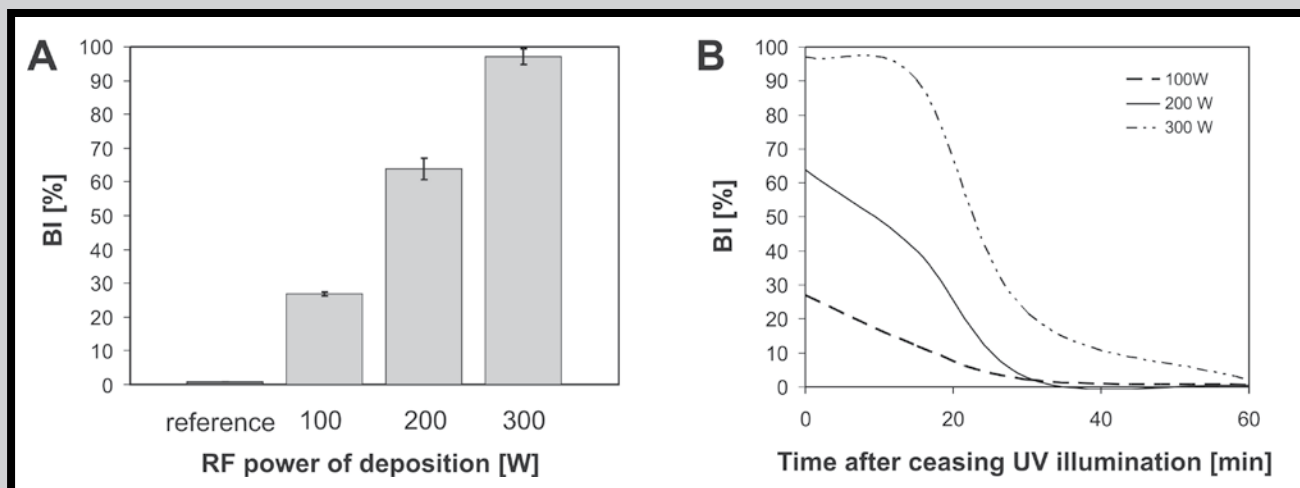
FIG. 4. Bactericidal effect BI of titanium oxide films deposited at different RF power input (A), and the dynamics of BI changes after ceasing UV illumination.

TABLE 1. The water contact angle and methylene iodide contact angle for titanium oxide films deposited at different power of deposition.

Deposition power [W]	Water contact angle before UV irradiation [deg]	Water contact angle after UV irradiation [deg]	Reduction of water contact angle [deg]	Methylene iodide contact angle before UV irradiation [deg]	Methylene iodide contact angle afterUV irradiation [deg]
100	92.5 ± 3.2	66.8 ± 2.7	25.7	$54.1 \pm 0,8$	$48.7 \pm 2,1$
200	91.8 ± 6.1	54.8 ± 2.6	37.0	$54.9 \pm 0,9$	$32.0 \pm 2,3$
300	95.6 ± 4.5	41.7 ± 2.7	53.9	$57.5 \pm 0,8$	$14.6 \pm 0,9$

TABLE 2. Values of surface free energy before and after UV illumination of the films deposited at different power of deposition.

Deposition power [W]	Free surface energy [mJ/m²]	
	before UV illumination	after UV illumination
100	18.4	41.7
200	17.9	54.6
300	15.6	68.1

Adhesion measured by means of scratch tests showed that the higher was the power of deposition, the stronger was the samples' adhesion. As it is shown in FIG. 3, for the layer deposited at 100 W delamination started under load of about 3 N, while for 200 W sample the layer lost its adhesion under the load of about 5 N. The best results were obtained for the sample deposited at 300 W, where delamination started at 8 N. The reason for this behavior may be a result of an increasing bonding force between substrates and a layer, due to the more intensive ion bombardment during the deposition, and perhaps also a growing thickness of the coatings.

Titanium oxide films synthesized in this work were subjected to bactericidal testing. In the study condition of experiment UV irradiation alone caused the death of 2% of the population of bacteria on uncoated glass which was the reference in this test. Titanium oxide coated surfaces revealed much higher BI in the same condition of irradiation.

The percentage of bactericidal inhibition BI for a series of titanium oxide coatings, deposited at different magnitudes of the RF power input, is shown in FIG. 4A. When irradiated under the same conditions, titanium oxide coated surfaces produced a much higher bacteria death rate, and this rate was an increasing function of the RF power of the oxide deposition. As a result, irradiation of the sample deposited at RF power of 300 Watt kills about 98% of all the bacteria.

The dynamic changes of bactericidal effect from the moment of switching off the UV illumination are presented in FIG. 4B. During the first 15 min BI coefficient was decreasing very slowly in all the three cases, i.e. all three films were the most active for about 15 min after the end of irradiation. Between 15 and 30 min there was the most sudden decrease of BI and the state before irradiation was reached after 60 min. The best results were obtained for the layer deposited at 300 Watt.

The UV-light induced hydrophilicity of the films deposited at 100, 200, and 300 W of RF power was investigated by measurements of the water contact angle (TABLE 1).

The values of water contact angle on RF PECVD titanium oxide films before UV irradiation were about 90° and were rather independent of the power of glow discharge. However, irradiation with UV light reduced this value by 53.9° for the film prepared at 300 W, and by 37° and 25.7° for samples deposited at 100 and 200 W, respectively. It should be noted, however, that the surface of the films is not completely wetted even after an irradiation. After the UV irradiated films were placed in the dark for 24 h, wettability of the surface was measured again using a new water droplet and the values of contact angle of approximately 90° were achieved again. The surface hydrophobicity of a solid surface is determined by its free surface energy. Free surface energy, calculated from the Owen's model, before and after the irradiation is presented in TABLE 2. The value of surface energy for the layer (100-300 W) before irradiation decreases from 18.4 to 15.6 mJ/m² and after irradiation increases from 41.7 to 68.1 mJ/m².

Conclusions

It was found that RF PECVD films are amorphous in the range of RF input power from 100 W to 300 W. The bactericidal activity and wettability of amorphous TiO_2 thin films were investigated. The best result of values of bactericidal inhibition of our films for the RF PECVD material, obtained in this work, amounted to 98%. Those films were still active for about 15 min after the end of irradiation, while stored in the dark. The initial values of BI the films were reached after 60 min. As far as the water wettability of our films is concerned, the contact angle, initially 92-96°, after 110 minutes of UV illumination decreased by 25.7, 37 and 53.9° for coatings deposited at 100, 200, 300 W, respectively.

The present study clearly indicates that the plasma deposited amorphous TiO_2 is a promising material for antibacterial and self-cleaning coatings.

References

[1] Carp O., Huisman C.L., Reller A.: Photoinduced reactivity of titanium dioxide. Prog. Solid State Ch. Vol. 32, 2004, pp. 33-177.

[2] Diebold U.: Structure and properties of TiO_2 surfaces: a brief review, Applied Physic, Vol. A 76, 2002, pp. 1-7.

[3] Macleod H.A.: Thin film optical filtres. MacMillan New York: 2nd edition ed., 1986.

[4] Leng X.Y., Huang N., Yang P., Chen J.Y., Sun H., Wang J., Wan G.J., Tian X.B., Fu. R. K.Y., Wang L.B., Chu P.K.: Structure and properties of biomedical TiO_2 films synthesized by dual plasma deposition, Surface and Coatings Technology, Vol. 156, 2002, pp. 295-300.

[5] Mills A, Lee S.K.: A web-based overview of semiconductor photochemistry-based current commercial application. J. Photoch. Photobiol. A: Chem. Vol. 152, 2002, pp. 233-247.

[6] Herrmann J.M: Heterogeneous photocatalysis: fundamental and application to the removal of various types of aqueous pollutants. Catal. Today vol. 53, 1999, pp.115-129.

[7] Fujishima A, Honda K.: Photolysis of water at a semiconductor electrode. Nature, Vol. 238, 1972, pp. 37-40.

[8] Wang R., Hoshimoto K., Fujishima A, Chikuni M., Kojima E., Kitamura A: Light-induced amphiphilic surface. Nature, vol. 388, 1997, pp. 431-432.

[9] Sakkas V.A., Arabatzis I.M., Konstantinou I.K., Dimou A.D., Albanis T.A., Falaras P.: Metachlor photocatalytic degradation using TiO_2 photocatalysts. Appl. Catal. B: Environ., Vol. 49, 2004, pp. 195-205.

[10] Chen J., Eberlein L., Langford C.H.: Pathways of phenol and benzene photooxidation using TiO_2 supported on zeolite. J. Photoch. Photobio. A: Chem., vol. 148, 2002, pp. 183-189.

[11] Dorfman LM, Adams GE: Reactivity of the hydroxyl radical in aqueous solutions. U.S. Department of Commerce, National, Bureau of Standards, NSRDS-NBS no. 46, 1972.

[12] Saito T., Iwase T, Horie J., Morioka T.: Mode of photocatalytic bactericidal action of powdered semiconductor TiO_2 on mutans streptococci. J. Photoch. Photobio. A: Chem. Vol. 14, 1992, 369-379.

[13] Matsunaga T., Tomoda R. , Nakajimia T., Nakamura N., Komine T.: Continuous sterilization system that uses photosemiconductor powders. Appl. Environ. Microbiol. Vol. 54, 1988, 1330-1333.

[14] Huang N., Xiao Z., Huang D., Yuan Ch: Photochemical disinfection of Escherichia coli with a TiO_2 colloid solution and a self-assembled TiO_2 thin films, Supramolecules Sciences, Vol. 5, 1998, pp. 559-564.

[15] Guo B., Liu Z., Hong L., Jiang H.: Sol-gel derived photocatalytic porous TiO_2 thin films. Surf. Coat. Technol., Vol. 198, 2005, pp. 24-29.

[16] Zhang X., Zhau M., Lei L.: TiO_2 photocatalyst deposition by MO-CVD on activated carbon. Carbon, Vol. 44, 2006, pp. 325-333.

[17] Sirghi L., Hatanaka Y., Aoki T.: Photocatalytic chemisorption of water on titanium dioxide thin films obtained by radio frequency magnetron deposition. Appl. Surf. Sci. Vol. 244, 2005, pp. 408-411.

[18] Miki-Yoshida M., Collins-Martinez V., Amčzaga-Madrid P., Aquilar-Elgučzabal A.: Thin films of photocatalytic TiO_2 and ZnO deposited inside a tubing by spray pyrolysis. Thin Solid Films, Vol. 419, 2002, pp. 60-64.

[19] Kolen`ko Y.U., Churagulov B.R., Kunst M., Mazerolles L., Colbeau-Justin C.: Photocatalytic proporties of titania powders prepared by hydrothermal method Appl. Catal. B: Environ. Vol. 54, 2004, pp. 51-58.

[20] Yasuda H.: Plasma Polymerization, Academic Press INC Orlando, 1985.

[21] Maeda M. and Watanabe T.: Evaluation of photocatalytic properties of titanium oxide films prepared by plasma-enhanced chemical vapor deposition. Thin Solid Films, vol. 489, 2005, pp. 320-324.

[22] Battiston G.A., Gerbasi R, Gregori A., Porchia M., Cattarin S., Rizzi G,A.: PECVD of amorphous TiO_2 thin films: effect of growth temperature and plasma gas composition. Thin Solid Films, vol. 371, 2000, pp.126-131.

[23] Sirghi L., Hatanaka Y.: Hydrophilicity of amorphous TiO_2 ultra-thin films. Surf. Sci., Vol. 530, 2003, pp. L323-L327.

[24] Karuppuchamy S., Jeong J.M.: Super-hydrophilic amorphous titanium dioxide thin film deposited by cathodic electrodeposition. Mater. Chem. Phys., Vol. 93, 2005, pp. 251-254.

[25] Owens D.K., Wendt R.S.: Estimation of the surface free energy of polymers. J. Appl. Polym. Sci., Vol. 13, 1969, pp. 1741-1747.

[26] Ohsaka T, Izumi F, Fujiki Y.: Raman Spectrum of Anatase TiO_2. J. Raman Spectrosc., Vol. 7, 1978, pp. 321-324.

[27] Porto S.P.S, Fleury P.A., Damen T.C.: Raman Spectra of TiO_2, MgF_2, ZnF_2, FeF_2 and MnF_2. Phys. Rev. Vol. 154, 1967, pp. 522-526.

[28] Bersani D, Lottici P.P., Ding X.Z.: Phonon confinement effect in the Raman scattering by TiO_2 nanocrystals, Appl. Phys. Lett., Vol 72, 1998, pp. 73-75.

[29] Djaoued Y, Brüning R., Bersani D., Lottici P.P., Badilescu S., Mat. Lett., Vol. 58 2004, pp. 2618.