THE IMPACT OF WORKING GAS ON PHASE COMPOSITION AND MICROSTRUCTURE TiO_2 COATING PREPARED BY REACTIVE MAGNETRON SPUTTERING

KACPRZYŃSKA-GOŁACKA Joanna[1], OSUCH-SŁOMKA Edyta[1], WIECIŃSKI Piotr[2], GARBACZ Halina[2], SKOWROŃSKI Jarosław[1], KOWALIK-KLIMCZAK Anna[1], SMOLIK Jerzy[1], MAZURKIEWICZ Adam[1]

[1] Institute for Sustainable Technologies - National Research Institute, Radom, Poland, EU
[2] Warsaw University of Technology, Warsaw, Poland, EU
[1]joanna.kacprzynska-golacka@itee.radom.pl

Abstract

Titanium dioxide (TiO_2) is one of the most useful materials in various applications related to catalysis, electronics, photonics, sensing, and medicine. TiO_2 is characterized by high chemical stability, outstanding optical and electrical properties, a non-toxic nature, and ease of mass production, and this is what causes it to be successfully used as a photocatalyst in many fields such as anti-bacterial applications, water purification, the decomposition of various organic pollutants, and solar cell applications TiO_2 thin films can be prepared by a variety of methods, such as the sol-gel method, pulsed laser deposition, chemical vapour deposition, spray pyrolysis, and sputtering techniques. The magnetron sputtering method can produce highly homogeneous films characterized by good adhesion to the substrate. This method also offers the advantage of depositing films on a large scale area, which makes it suitable for industrial applications. TiO_2 coatings prepared by magnetron sputtering method have two types of crystallographic structures: rutile and anatase, which are characterized by difference properties. For example, anatase can be characterized by better photocatalytic properties, while rutile has a higher absorbance property than anatase. Depending on the contribution of particular phases in the crystalline structure, the TiO_2 coating is characterized by different functional properties. The article presents the influence of the chemical composition of the process atmosphere on phase composition TiO_2 coatings obtained by reactive magnetron sputtering. The research methods also include the microstructure and the mechanical properties analysis of the obtained coating.

Keywords: Titanium dioxide, magnetron sputtering, PVD

1. INTRODUCTION

Titanium dioxide (TiO_2) is characterized by high chemical stability, outstanding optical and electrical properties, a non-toxic nature and ease of mass production [1]. It is also a very good catalyst used in many application areas [2,3]. One of the main photocatalytic properties of titanium dioxide (TiO_2) is its ability to self-purify [4]. Due to the fact that, under the influence of light on its surface, there are oxidation processes and decomposition reactions of organic compounds, various types of contaminants fall off or easily or can be rinsed with water by spaying or immersion. In addition, titanium dioxide exhibits strong bactericidal properties [5], which intensify under the influence of UV radiation. TiO_2 is also a strongly hydrophilic material [6]. The contact angle of water with glass coated with titanium dioxide can be up to several degrees. This low water wetting angle makes these coatings can be successfully used to improve the filtration properties of membranes used in water filtration processes, which have to be characterized by hydrophilicity in addition to bactericidal and anti-biofouling properties. The state of the art has shown that the properties of TiO_2 coatings depend, among other things, on the phase composition [7]. TiO_2 coatings may have three types of crystallographic structures: brooklite, rutile, and anatase, which are characterized by difference properties. For example, anatase is characterized by better photocatalytic properties, while rutile has a higher absorbance property than anatase. Depending on the contribution of particular phases in the crystalline structure, the TiO_2 coating will be characterized by different functional properties. TiO_2 thin films can be prepared by a variety of methods such as the sol-gel method, pulsed laser deposition, chemical vapour deposition, spray pyrolysis, and sputtering techniques [1, 7, 8, 9]. The magnetron sputtering method can produce highly homogeneous films characterized by good adhesion to the substrate. This method also offers the possibility of forming the phase structure according to the technological parameters of the process [10, 11].

2. EXPERIMENT

2.1. Thin film preparation

TiO_2 thin films were deposited by the magnetron sputtering method. The samples were made of pure iron (Armco). The substrates were mechanically polished using abrasive paper 1000, and chemically cleaned in a trichloroetylen (CHCl) ultrasonic bath. The PVD coating deposition process was executed with the use a device produced by the Institute for Sustainable Technology - National Research Institute in Radom (ITeE-PIB Radom). A pure titanium target (99.99 %) with a 160 mm diameter was used as a sputter target. The gases used are pure argon (99.99990 %) as the sputtering gas and pure oxygen (99.99 %) as the reactive gas. All the samples were fixed on the substrate holder, and the distance between the target and the substrate holder was set to 120 mm. The target was continuously cooled by water. Before each deposition, the sputtering chamber was evacuated down to a pressure of 5.5×10^{-5} mbar, then argon and oxygen gases were introduced at constant flow rates. The rate of oxygen flow was varied (5 %, 8 %, 12 %, 15 %), whereas all other deposition parameters were kept constant. The discharge was generated at a constant DC power of 1300 W. The deposition time was fixed at 240 min. The voltage applied to the substrate was 0 and the working gas pressure was 5×10^{-3} mbar.

2.2. Thin film characterization

The microstructure and surface morphology of the TiO_2 coatings were characterized with the use of SU-70 Hitach scanning microscope. The microstructure observations were carried out on a properly prepared sample in the form of brittle fracture. The thicknesses of the coatings were carried out on metallographic samples mechanically polished applying Struers equipment and technique. To investigate the structure of obtained films, a Bruker D8 Discover diffractometer was used in Bragg-Brentano geometry (θ-2θ geometry), at room temperature with Co Kα radiation. The mechanical properties of the films, such as hardness and Young's modulus, were investigated using the CSM Instrument nanoindenter equipped with a Berkovich diamond indenter tip. The indenter was operated in the continuous stiffness mode with a maximum load of 100 mN. The applied load is 3 mN. The wettability of the samples was studied using equipment produced by ITeE-PIB in Radom. An average value of the contact angle between the sample surfaces and a minimum of two deionized water drops was measured using the sessile drop method. The static contact angle was obtained analysing the captured images using the Tangent Method 1 algorithm [12].

3. RESULTS

3.1. Material characterization of TiO_2 coatings.

The main target of this study is analyse TiO_2 thin film phase structures prepared with different rates of oxygen in the chemical composition of the working atmosphere. The crystal structure of the films is shown in **Figure 1**. The XRD patterns indicate that the samples prepared in the working atmosphere with the lowest oxygen content (5 %) were characterized by structure composed by anatase, brooklite, and rutile. Increasing the oxygen content to 8 % in the chemical composition of the working atmosphere resulted in a significant increase the anatase fraction in the phase structure of the coating. From the results of XRD measurement, it can be noticed that, when the oxygen contents were higher (12 and 15 %), the obtained TiO_2 coating was composed of only the anatase phase. Thus, it is clear that the crystal formation is influenced by the chemical composition of the working atmosphere.

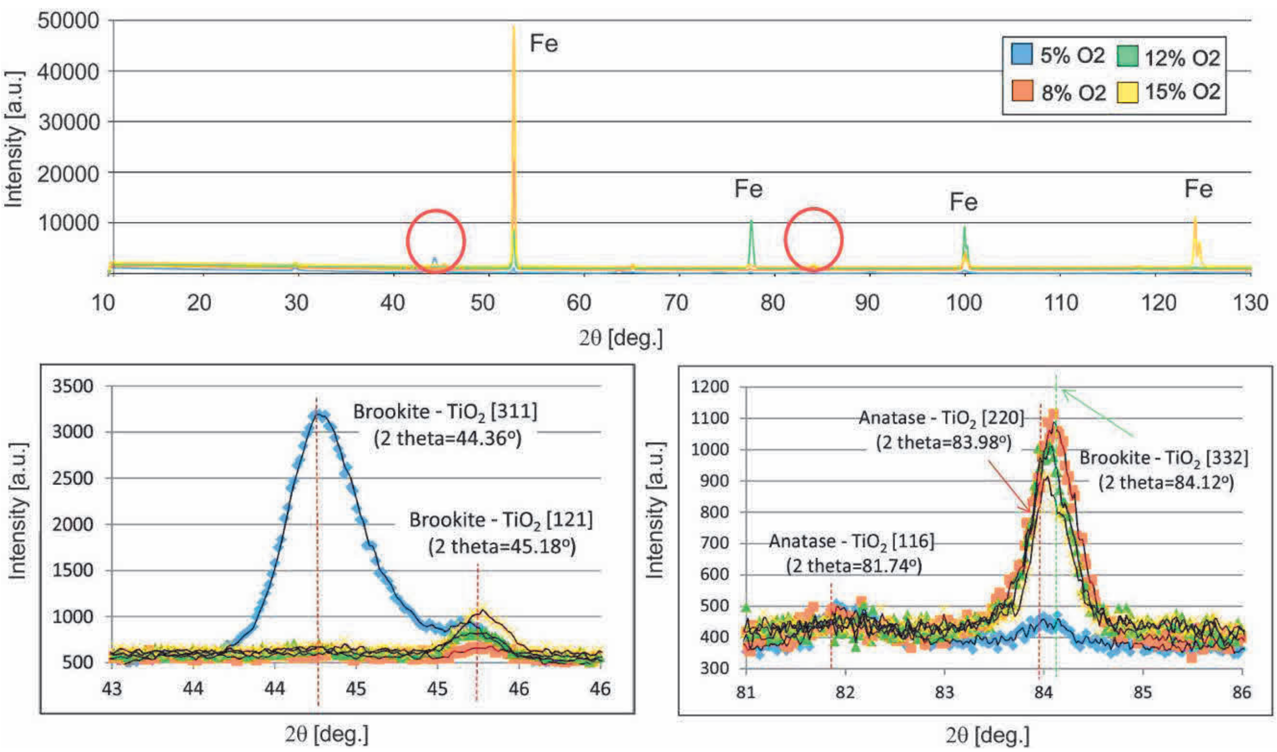

Figure 1 XRD patterns of TiO_2 coatings deposited in different O_2 content in gas atmosphere

The analysis of the microstructure of coatings prepared using different working atmospheres indicated significant differences in their structural construction (**Figure 2**). The coating prepared in the working atmosphere with the lowest oxygen content (5 %) was characterized by a very irregular, porous structure (**Figure 2a**). Increasing the oxygen content to 8% in the chemical composition of the working atmosphere resulted a significant refinement with a densely packed, non-porous, homogeneous structure of the coatings (**Figures 2b, c, d**). Cross sectional analysis revealed significant differences in coating thicknesses despite the same deposition times (**Figure 3**). These differences may be due to the "poisoning" of the magnetron source during the process producing a decrease in the intensity of the deposition. Increasing the oxygen content in the working atmosphere by only 10% resulted in almost a 10-fold decrease in the film thickness (**Figures 3a, d**). Cross-section SEM images showed that thin films prepared in a gas atmosphere with 8 %, 12 %, 15 % content of O_2 were nanocrystalline with crystallite sizes in the range from 30 nm to 50 nm (**Figures 3b, c, d**). Only the TiO_2 coating prepared with the lowest content of O_2 was microcrystalline with a crystallite size of about 0.5 µm (**Figure 3a**).

Table 1 Mechanical properties of TiO_2 coatings

Type of coating Composition of working atmosphere	L1 - TiO_2 (5%O_2+95%Ar)	L1 - TiO_2 (8%O_2+92%Ar)	L1 - TiO_2 (12%O_2+88%Ar)	L1 - TiO_2 (15%O_2+85%Ar)
Hardness (GPa)	6.0	5.0	5.5	6.5
Young modulus (GPa)	125	127	130	610
Roughness (µm)	0.300	0.039	0.030	0.015

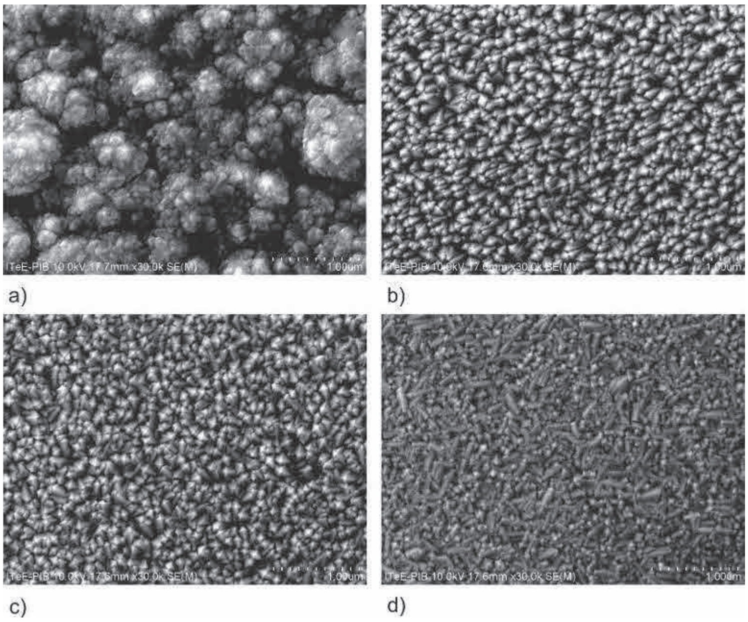

Figure 2 SEM images of the microstructure and morphology of the TiO_2 coatings deposited in different O_2 contents of the working atmosphere: a) 5 % O_2, b) 8 % O_2 c) 12 % O_2, and d) 15 % O_2

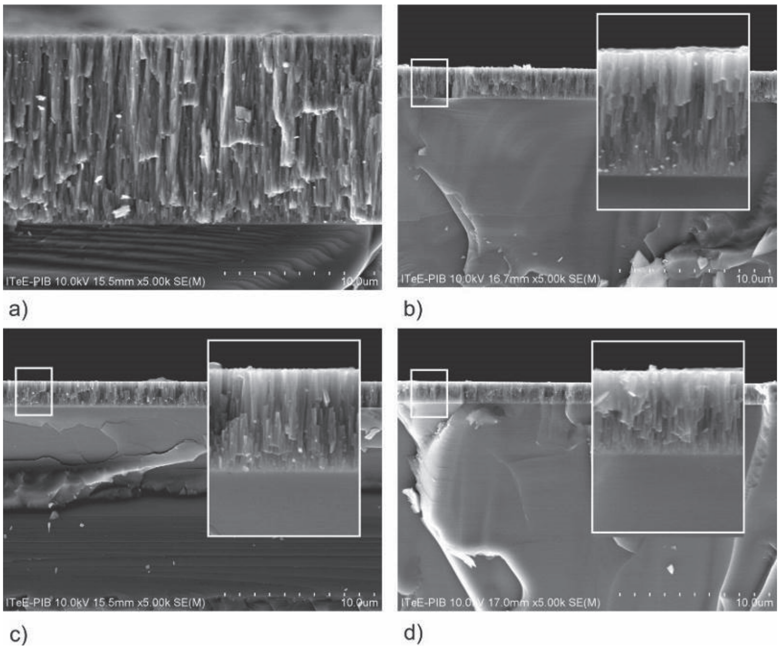

Figure 3 Cross-section of SEM images of TiO_2 thin films deposited in different O_2 contents of working atmospheres: a) 5 % O_2, b) 8 % O_2 c) 12 % O_2, d) 15 % O_2

The effect of increasing the proportion of oxygen in the gas atmosphere to significantly reduce the surface roughness of the obtained coatings is also observed (**Table 1**). The roughnesses of TiO_2 thin films were Ra1 = 0.25 µm, Ra2 = 0.039 µm, Ra3 = 0.030 µm, and Ra4 = 0.015 µm for the films produced with the oxygen contents of 5 %, 8 %, 12 %, 15 %, respectively. Analysis of mechanical properties (**Table 1**) showed no significant differences between the tested coatings. All coatings were characterized by similar hardness and Young's modulus. Only in the case of a coating produced in a working atmosphere of 15 % O_2 and 85 % Ar, was a Young's modulus of 600 GPa noted.

3.2. Functional properties

TiO_2 is an outstanding photocatalytic material, which attracts many studies on the photocatalytic behaviour of TiO_2 thin films. In this study, water contact angle measurements were conducted to examine the UV-induced phenomena of the films. **Figure 4** shows the contact angles before and after UV illumination for the films obtained using different chemical compositions of the working atmosphere. Before UV light irradiation, the contact angles of TiO_2 thin film were 20˚ and 15˚ for the films with the oxygen contents in the chemical composition of the gas atmosphere of 5 % and 8 %, respectively. TiO_2 coating produced in gas atmosphere with higher contents of O_2 (12 % and 15 %) were characterized by significantly higher contact angles 40-45˚. TiO_2 is a hydrophilic material, where the contact angle of the flat dense TiO_2 layer is about 50-60˚. Therefore, it is reasonable to obtain a good hydrophilic TiO_2 thin film with a reactive sputtering process.

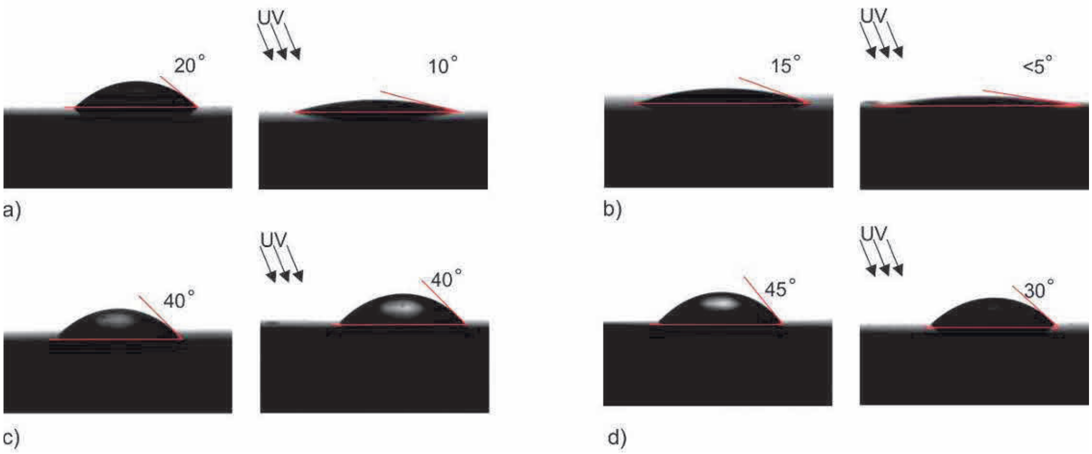

Figure 4 Wettability measurements results of TiO_2 thin films deposited in different O_2 contents in gas atmospheres: a) 5 % O_2, b) 8 % O_2 c) 12 % O_2, d) 15 % O_2

After 10 min of UV light irradiation, the thin films that were produce using a gas atmosphere with a low content of O_2 (5 % and 8 %) became super-hydrophilic. The contact angles were below <8˚ and revealed good photocatalytic wettability. For the other coatings, no significant change in the contact angle after UV irradiation was observed. The film thickness does not affect the hydrophilicity, because it is only related to the physical-chemical property of the film surface. The reason for this better photo-induced hydrophilic film is probably the phase structure on the surface. Layers consisting of an anatase-brooklite phase show a faster drop in the contact angle than did the anatase layers.

4. CONCLUSION

The DC reactive magnetron sputtering process without external substrate heating has been successfully used for the deposition of crystalline TiO_2 thin films with hydrophilic activity. TiO_2 thin films were deposited using magnetron sputtering with various chemical compositions of the working atmosphere. Other deposition conditions, such as sputtering power, pressure, and the distance between the target and substrates, were maintained constant in each process. Therefore, the influence of the sputtering gas atmosphere on microstructure, surface, and the mechanical and functional properties could be determined. Thin films prepared with O_2 ratios of 5 % and 8 % in the gas atmosphere had compositions of rutile, anatase, and brooklite phases. The other samples had only an anatase structure. Surface investigations revealed that all thin films were densely packed and consisted of nanocrystalline grains. Cross-sectional SEM images showed that thin films prepared in gas atmospheres with 8 %, 12 %, and 15 % content of O_2 were nanocrystalline with crystallite sizes in the range from 30 nm to 50 nm. Only the TiO_2 coating prepared with the lowest content of O_2 was microcrystalline with a crystallite size of about 0.5 μm. Due to the change of sputtering gas atmosphere, there was also a change in roughness. All deposited thin films were characterized by very good wettability. The wellcrystalline composition of anatase and brooklite TiO_2 thin films obtained in a gas atmosphere with 8 % content of O_2 exhibited the best hydrophilicity before and after UV irradiation. The TiO_2 thin film obtained in a gas atmosphere with a 5 % O_2 content was easily rendered to be super-hydrophilic after a short period of UV light irradiation. Layers that contain only the anatase phase show worse super-hydrophilicity than layers containing a composition mainly of the anatase and brooklite phases. The experiments demonstrated that magnetron sputtering is a convenient technique for the deposition of UV-induce hydrophilic TiO_2 thin films.

ACKNOWLEDGEMENTS

This work was supported by the National Centre for Research and Development in Poland carried out within the project LIDER VII „Multifunctional polymer membranes modified using hybrid technology of surface engineering", no. LIDER/31/0092/L-7/15/NCBR/2016

REFERENCES

[1] SUDA Y., KAWASAKI H., UEDA T., OHSHIMA T. Preparation of high quality nitrogen doped TiO_2 thin film as a photocatalyst using a pulsed laser deposition method. *Thin Solid Films*, 2004, vol. 453-454, pp. 162-166.

[2] ZHANG X., XIAO G., WANG Y., ZHAO Y., SU H., TAN T. Preparation of chitosan-TiO_2 composite film with efficient antimicrobial activities under visible light for food packaging applications. *Carbohydrate Polymers*, 2017, vol. 169, pp. 101-107.

[3] JOUANNY I., LABDI J.S., AUBERT P., BUSCEMA C., MACIEJAK O., BERGER M.H., GUIPONT V., JEANDIN M. Structural and mechanical properties of titanium oxide thin films for biomedical application. *Thin Solid Films*, 2010, vol. 518, pp. 3212-3217.

[4] YOU S.J., SEMBLANTE G.U., LU S.C., DAMODAR R.A., WEI T.C. Evaluation of the antifouling and photocatalytic properties of poly(vinylidene fluoride) plasma-grafted poly(acrylic acid) membrane with self-assembled TiO_2. *Journal of Hazardous Materials*, 2012, vol. 237-238, pp. 10-19.

[5] ADAMS L.K., LYON D.Y., ALVAREZ P. Comparative eco-toxicity of nanoscale TiO_2, SiO_2, and ZnO water suspensions. *Water Research*, 2006, vol. 40, pp. 3527-3532.

[6] STEVENS N., PRIEST C.I., SEDEV R., RALSTON J. Wettability of photoresponsive titanium dioxide surfaces. *Langmuir*, 2003, vol. 19, no.8, pp. 3272-3275.

[7] MUTUMA B.K., SHAO G.N., KIM W.D., KIM H.T. Sol-gel synthesis of mesoporous anatase-brookite and anatase-brookite-rutile TiO_2 nanoparticles and their photocatalytic properties. *Journal of Colloid and Interface Science*, 2015, 442, pp. 1-7.

[8] YU Q., WANG H., PENG Q., LI Y., LIU Z., LI M. Different toxicity of anatase and rutile TiO_2 nanoparticles on macrophages: Involvement of difference in affinity to proteins and phospholipids. *Journal of Hazardous Materials*, 2017, 335, pp. 125-134.

[9] ZYWITZKI G.O., MODES T., SAHM H., FRACH P., GOEDICKE K., GLÖß D. Structure and properties of crystalline titanium dioxide layers deposited by reactive pulse magnetron sputtering. *Surface & Coatings Technology*, 2004, vol. 180-181, pp. 538-543.

[10] XIE W., JIAO S., WANG D., GAO S., WANG J., YU Q., LI H. The effect of sputtering gas pressure on the structure and optical properties of MgNiO films grown by radio frequency magnetron sputtering. *Applied Surface Science*, 2017, vol. 405, pp. 152-156.

[11] SMOLIK J., MAZUKIEWICZ A., KACPRZYŃSKA-GOŁACKA J., RYDZEWSKI M., SZOTA M., MIZERA J. Composite layers "Mg-Al intermetalic layer / PVD" coating obtained on the AZ91D magnesium alloy by different hybrid surface treatment methods. *Archives of Metallurgy and Materials*, 2015, vol. 60, pp. 1031-1035.

[12] KWOK D.Y., NEUMANN A.W. Contact angle measurement and contact angle interpretation. *Advances in Colloid and Interface Science*, 1999, vol. 81, pp. 167-249.