Preparation of porous TiO$_2$ films by means of pulsed laser deposition for photocatalytic applications

A. Iwulska[*] and G. Śliwiński,

Polish Academy of Sciences, IF-FM, Photophysics Dpt., 14 Fiszera St., 80-231 Gdańsk, Poland

Abstract—In this work the preparation and structure properties of porous thin films of TiO$_2$ were investigated. The films were produced by means of the pulsed laser deposition technique using laser pulses at 266nm (10Hz) and at fluencies of 1–3.5J/cm^2. The process was performed in vacuum using O$_2$ buffer gas and films were deposited on the SiO$_2$ glass or Si substrate. X-ray diffraction (XRD) and Raman analysis of the structure and chemical composition of the obtained samples confirmed the presence of both anatase and rutile phase. For the O$_2$ pressure applied above 10^{-2} hPa, the anatase bands were observed and below this value, rutile bands dominated in the Raman spectra in agreement with XRD data.

It is well known that the photoelectrochemical properties of titanium dioxide nanostructures are associated with its ability to absorb light. TiO$_2$ absorbs mainly in the ultraviolet and only a few percent of the spectrum falls into the visible range. This is a serious limitation from the point of view of numerous applications such as photovoltaic, photocatalysis [1-5], etc. An extension of the range of TiO$_2$ absorption towards the visible range is of much interest and stimulates research on this topic. The titanium dioxide occurs in nature in three polymorphic phases: anatase, rutile, and brookite. The rutile phase is thermodynamically the most stable form of titanium dioxide. Both anatase and brookite undergo a phase change into rutile around 700-800°C, and the transformation is irreversible [6-8]. TiO$_2$ thin films may be deposited by different deposition techniques. In the case of the TiO$_2$ nanostructures prepared by methods based on the physical vapour deposition, the resulting structure is the product of vapour crystallisation on the substrate surface [9-13]. In particular, during Pulsed Laser Deposition (PLD) the particles are produced by laser ablation of the target. The results obtained by means of PLD show that ambient oxygen pressure influences strongly optical, mechanical and structural properties of the films [9, 14]. Kim and coworkers reported the dominant rutile phase and the presence of anatase only for a very narrow range of O$_2$ pressure applied [8]. High quality TiO$_2$ thin film was grown at the O$_2$ pressure of 1.33–13.3Pa and at high substrate temperature (700°C). From the study of the crystalline characteristic of the as-grown films investigated as a function of the oxygen pressure and film thickness follows that for increasing film thickness the integrated intensity of the rutile peaks remains constant, whereas the content ratio of anatase to rutile increases [5]. The effect of pressure is also reported for the TiO$_2$-layers deposited by reactive dc-sputtering and high-power pulsed magnetron sputtering at various oxygen and argon pressures [15, 16]. With an increasing sputtering pressure the microstructure of the produced films modifies significantly and the deposited crystal phases change from rutile to anatase.

In this work the porous thin films of TiO$_2$ for investigation of the photocatalytic activity were produced using the PLD method. The chemical composition and the structure of the nano-structured samples investigated by means of the Raman and energy-dispersive X-ray (EDX) spectroscopic techniques, X-ray diffractometry (XRD), and obtained from the scanning electron microscope (SEM) observations were analyzed and discussed.

The scheme of the experimental arrangement is shown in Fig. 1. A pulsed Nd:YAG laser (Quantel: λ=266nm, rep. rate 10Hz, pulse duration 6ns) was used to ablate the pure (99.7%) TiO$_2$ target. The laser was operated at fluencies of 1–3.5J/cm^2. For sample production the deposition chamber was evacuated previously to a base pressure below 2·10^{-3}Pa and filled with oxygen gas to pressures ranging from 0.01 to 1Pa. The SiO$_2$ glass or Si substrates were set 5cm apart from the target and kept at a temperature of 500°C during deposition. After deposition samples were annealed at the same temperature and oxygen pressure for half an hour.
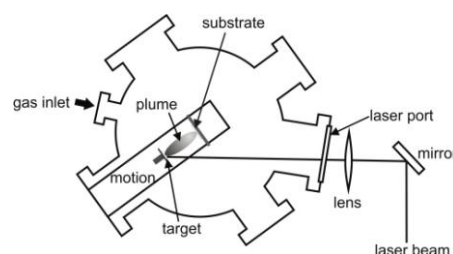

Fig. 1. The scheme of the experimental setup.

[*] E-mail: aiwulska@imp.gda.pl

The Raman spectra were recorded by a confocal micro-Raman spectrometer (InVia, Renishaw) with sample excitation by means of an green argon ion laser emitting at 514nm. Crystalline phases were investigated by means of X-ray diffraction (XRD) using the X'Pert (Philips) diffractometer. XRD patterns were recorded under excitation by the Cu K_α line at room temperature. The study of surface topography and elemental analysis were performed by means of the scanning electron microscope EVO-40 (Zeiss) coupled with the Quantax 400 EDX XFlash 5010 apparatus.

The dependence of the Raman spectra of TiO_2 thin films on the O_2 pressure in a range from $5.4 \cdot 10^{-2}$ to 1.2 Pa is shown in Fig. 2. The rutile crystalline phase of TiO_2 dominates at low pressures and with the deposition pressure increasing up to 1.2Pa an increase of the anatase content is observed in agreement with literature data. It is worth mentioning that for samples prepared at pressures below the range discussed above the formation of TiO_2 structures was not observed and only a Ti layer formed on the substrate.
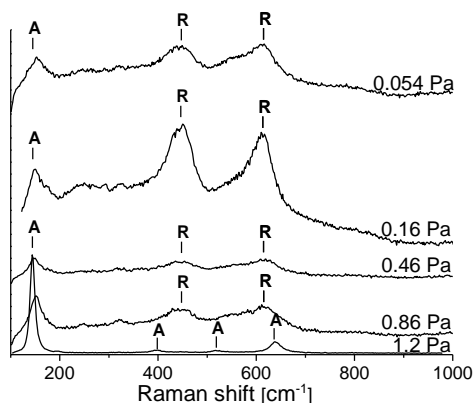

Fig. 2. The pressure dependence of the anatase (A) and rutile (R) Raman band intensities.
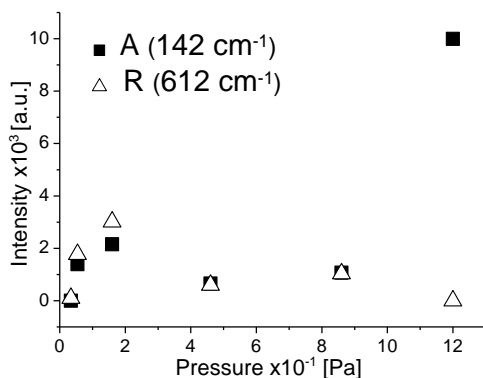

Fig. 3. The pressure dependent intensities of the characteristic Raman bands of anatase (A) and rutile (R) centred at 142 cm^{-1} and 612 cm^{-1}, respectively.

For low oxygen pressures the ratio of phase contents remains nearly constant and the sharp increase of the anatase band intensity at pressures around 1Pa indicates a possible threshold of the pressure dependent preparation process – see Fig. 3.

The XRD analysis shows for all studied samples the peaks from both anatase and rutile together with the Si band ascribed to the substrate. However, the pressure dependent evolution of the crystalline phases becomes evident from observation of the XRD spectra obtained for samples deposited at two pressure values of 0.16 and 1.2 Pa, which is shown in Fig. 4. The spectrum is dominated by rutile bands for samples prepared at 0.16Pa. In the case of an elevated pressure of 1.2Pa the spectral structure is mainly composed of several strong anatase peaks. The coincidence of the XRD and Raman data can be concluded from comparison of Figs. 2-4. This leads further to the conclusion that in the case of TiO_2 samples prepared by the PLD technique, the crystalline phase composition as well as structure of the films depend on the deposition pressure, similarly to the results obtained by other techniques.
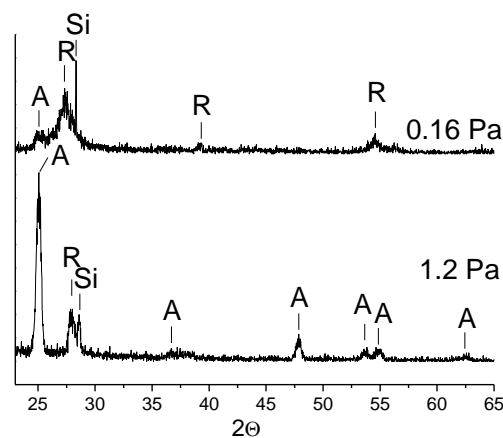

Fig. 4. The XRD spectra of films deposited at pressure of 0.16 and 1.2 Pa; A, R and Si corresponds to anatase, rutile and silicon.

From the EDX analysis the mole fractions of elements contained in the layer and substrate were determined. In the sample deposited at a pressure of 1.2 Pa the content of titanium, oxygen and silicon was equal to 28% wt., 37% wt., and 12% wt. respectively, while that of the other elements included in the glass (Na, Mg, Ca, K) was 23% wt. In the case of a sample deposited at lower pressure (0.46 Pa) contents of 7% wt., 40% wt., 20% wt., and 33% wt. were measured, respectively – see Tab. 1.

Table 1. The EDX data of the mole fractions of elements contained in the layer and substrate.

p [Pa]	Ti [wt. %]	O [wt. %]	Si [wt. %]	Other [wt. %]
0.46	7	40	20	33
1.2	28	37	12	23

The film thickness within a range of 0.61-1.24μm was obtained from the data in Fig. 5b. Estimation was based on the SEM-EDX line scans of the sample cross-section. The sample SEM image of the film produced at a pressure of 0.46Pa on the glass substrate and the corresponding EDX line scan are shown in Fig. 5a and b.

Local thickness differences observed in the image result most probably from the lack of homogeneity of the particle distribution in the cloud of ablated material, which in turn is reflected in the local deposition rates. This conclusion was confirmed by different values of film thickness depending on the place where the measurement was made.
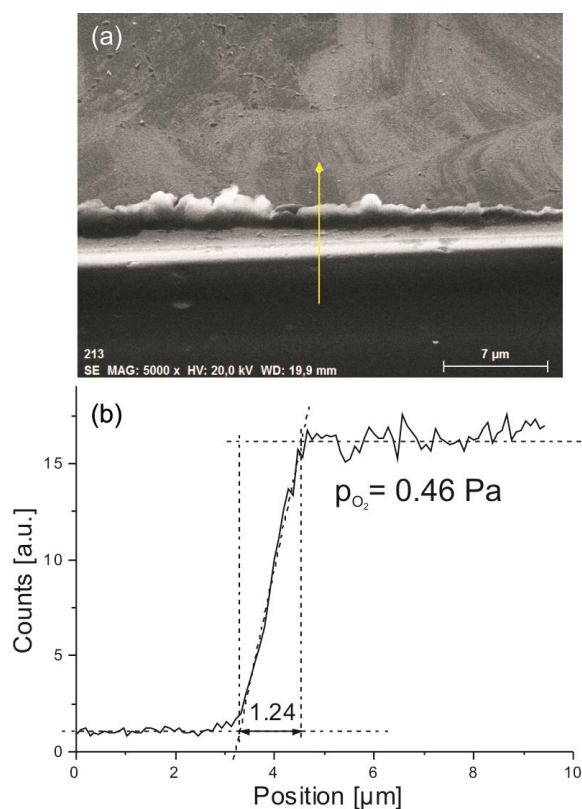

Fig. 5. The SEM image of the sample deposited at 0.46 Pa (a), and EDX line scan of Ti by cross-section of the sample (b).

In summary, the porous TiO_2 films were prepared by means of PLD of the material ablated from pellet. The results show the interaction of evaporated Ti particles with TiO_2 target and O_2 gas. The dependence of the buffer gas pressure O_2 on the ratio of the anatase and rutile crystalline phase contents was studied by spectroscopic techniques. The pressure effect was concluded from the coincidence of μ-Raman and XRD spectral data. At a pressure of less than 1Pa, layers consisting mainly of the rutile phase were produced, and at slightly elevated pressure, the anatase content dominated. The result was additionally confirmed by quantitative EDX measurement. The variation in the film thickness obtained from EDX line scans was ascribed to the local conditions on the substrate and indicated by inhomogeneous distribution of particles during deposition.

The work is in progress in order to precise the conditions of reproducible and stoichiometric preparation of samples.

References

[1] B. Ohtani, J. Photochem. Photob. C: Photochem. Rev. **11**, 157 (2010).
[2] D. Robert, S. Malato, Sci. Tot. Envir. **291**, 85 (2002).
[3] A. Fujishima, T.N. Rao, D.A. Tryk, J. Photochem. Photobio. C: Photochem. Rev. **1**, 1 (2000).
[4] M.F. Brunell *et al.,* Thin Solid Films **515**, 6309 (2007).
[5] M. Terashima, N. Inoue, S. Kashiwabara, R. Fujimoto, Appl. Surf. Sci. **169-170**, 535 (2001).
[6] E. Kociołek-Balawajder, M. Szymczyk, Przemysł Chemiczny **86**/12 (2007).
[7] D.A.H. Hanaor, Ch.C. Sorrell, J. Mater. Sci. **46**, 855 (2011).
[8] J.-H. Kim, S. Lee, H.-S. Im, Appl. Surf. Sc., **151** 6 (1999).
[9] F. Di Fonzo *et al.,* Nanotechnology, **20**, 1 (2009).
[10] R.W. Kelsall *et al., Nanotechnologie*, (Warszawa, PWN 2008)
[11] Y. Xu and M. Shen, J. Mater. Process. Technol. **202**, 301 (2008).
[12] P.M. Martin, *Handbook of Deposition Technologies for Films and Coatings - Science, Science, Applications and Technology* (Elsevier 2010).
[13] S. Yamamoto et al., Thin Solid Films **401**, 88 (2001).
[14] Y. Shen *et al.,* Opt. and Las. Tech. **40**, 550 (2008).
[15] T. Tölke, A. Kriltz, A. Rechtenbach, Thin Solid Films **518**, 4242 (2010).
[16] V. Stranak *et al.*, J. Phys. D: Appl. Phys. **41**, 055202 (2008).