

PROPERTIES OF SOL-GEL TiO₂ LAYERS ON GLASS SUBSTRATE

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TiO₂ thin layers were prepared on glass substrate by sol-gel process and dip-coating technique. The coating solution was prepared by using tetra-n-butyl orthotitanate (C₁₆H₃₆O₄Ti) precursor. Very stable sols of this oxide were synthesized using the alcoxide in the presence of acetic acid and using acetyl acetone as a chelating agent. The layers obtained were transparent with good adhesion to the soda-lime glass substrate. The optical absorbance and thickness of the layers as a function of the number of coatings were determined and their surface microstructures was observed by SEM. Absorbance spectra showed an increased absorbance of the layers in the range of 280 – 300 nm. Nanocrystalline anatase particles were detected in the films prepared by heating at higher temperatures. The thickness of layers varied from 80 to 200 nm depending on the coatings number. Corrosion of the substrate covered by the film was followed in demineralised water and was found to be somewhat lower in comparison with the original uncovered glass surface.

INTRODUCTION

Titanium dioxide layers on glass substrates have been widely studied for optical and electronic applications because they have a high refractive index, high photocatalytic activity and good physical and chemical stability [1]. There are three techniques developed for coating of TiO₂ onto the surface of the support, namely, impregnation, chemical vapour deposition (CVD) and sol-gel techniques [2]. Coating of TiO₂ by impregnation is widely used by most researches because the technique is easy and does not require any complicated equipment, but the TiO₂ coating is not homogeneous and it is easily detached from substrates. On the contrary, CVD and sol-gel techniques usually generate a relatively homogeneous TiO₂ coating.

The sol-gel method has the advantage of easy control of chemical composition of thin layers [3]. Titanium dioxide layers prepared by sol-gel method have been used for production of architectural windows [4, 5], as working electrodes in electrochromic devices (ECD) [6-13] and also for solar cell applications [14-21]. In the last decade, titanium oxide layers have been applied in nanocell photovoltaic systems [22-24] and as photocatalyst to remove organic pollutants from industrial air and water. Also, gas sensors, ultra filtration membranes and semiconductor devices can be based on sol-gel titania coatings [35].

The present work focuses on the study of the structure, optical and chemical properties of the TiO₂ layers prepared by the sol-gel method and deposited on glass surface by the dip coating technique. The TiO₂ layers

were characterized using UV-VIS spectrophotometer, XRD diffraction analysis and the thickness of the layers was measured with electron microscope. In addition, protective effect of the film against the corrosion of the substrate in demineralised water was determined.

EXPERIMENTAL

The TiO₂ layers were prepared using sol-gel method. Details of the procedure used in this work were described previously [25]. Tetra-n-butyl-orthotitanate was used as a precursor to prepare TiO₂ sol. A mixture of CH₃COOH, ethanol and acetyl acetone was added to tetra-n-butyl-orthotitanate and then was diluted by adding a mixture of ethanol and water under continuous magnetic agitation at room temperature. TiO₂ thin films were laid on optically transparent microscopy glass substrates by dip coating procedure. Before dip coating, the glass substrate was washed with demineralised water. The thermal treatment of the sample with deposited layer started by drying at 80°C for 2 h, followed by tempering at 550°C in air for 1 h and finished by cooling with the rate of 20-25°C/min.

Various techniques were used in order to characterize final properties of the layers. XRD analysis of the films on the quartz glass substrate was performed to determine modification of TiO₂ with respect to heating temperature and number of subsequent coatings on the substrate. The electron microscope Hitachi S-4200 was used to measure thickness of the layers and to examine the quality and microstructure of the films. A fracture of

the sample was prepared for these measurements allowing examining the surface of the layer along with the area perpendicular to this surface. Optical absorbance of the films deposited on glass substrates was measured by UV-VIS spectrophotometer (UV-1201 Shimadzu). Also refraction index of the layers was measured by means of ellipsometry technique. Static corrosion tests were performed by immersing of the samples into demineralised water, with starting *pH* value = 6.5 at 80°C for different times ranging from 10 minutes to 16 days. Three samples were immersed into 25 ml of demineralised water. The relation between the surface of the sample and volume of water *S/V* amounted 0.2439 m²/dm³. After the exposure time, liquid samples were filtered and analysed for their Na⁺ ions concentration. The concentration of Na⁺ ions extracted from the layers into demineralised water was determined using absorption atomic spectrophotometer and compared with the Na⁺ ions extracted from the original glass surface without a film.

RESULTS AND DISCUSSION

Electron microscopy of TiO₂ layers

The TiO₂ films that exhibited good adhesion to the glass substrate were transparent or translucent. This is not in agreement with Chul Han Kwon et al. [26] who reported that TiO₂ thin films do not show a good adhesion to the glass substrate when they are obtained on the glass substrates by dip-coating technique and heat treated at temperatures up to 500°C for 1 h. This holds especially if two consecutive coatings were used to prepare a thicker layer. They used titanium tetraisopropoxide (Dupont, USA) as the precursor for the synthesis of TiO₂ sol. Titanium tetra-isopropoxide solution was prepared by diluting with isopropyl alcohol subsequently peptised by stirring in the presence of water and nitric acid as a catalyst. The alcoxide and the other compounds used differ from ours, which might be together with relatively low heating temperature the reason for weak adhesion to the glass surface.

The thickness of the layers was measured using scanning electron microscopy. The thickness of the first coating is 88.3 nm, for two coatings is 106.3 nm and for three coatings was detected to be 201 nm. Figure 1 shows the surface and thickness of the layer consisting of one TiO₂ film. The layer prepared by two repeated depositions can be seen on the figure 2, and in figure 3 the layer prepared by three subsequent depositions is shown. Each subsequent film was submitted after deposition to the same heat treatment procedure as the first deposited film (550 C for 1 hour).

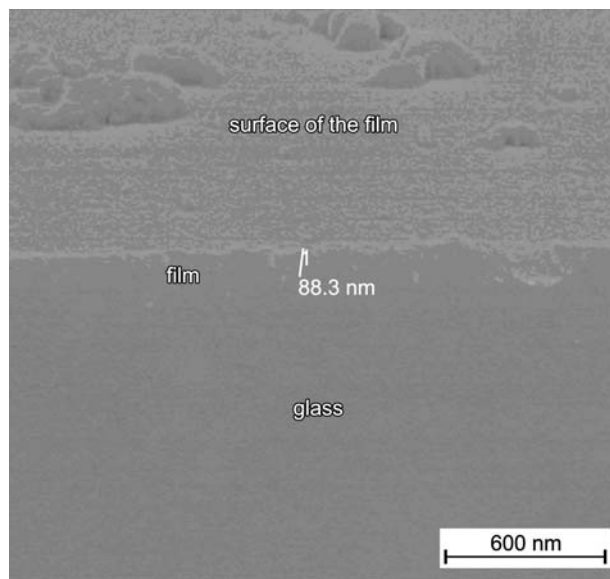


Figure 1. Surface and thickness of TiO₂ layer with one film on the slide glass (heating temperature 550°C, time 1 h).

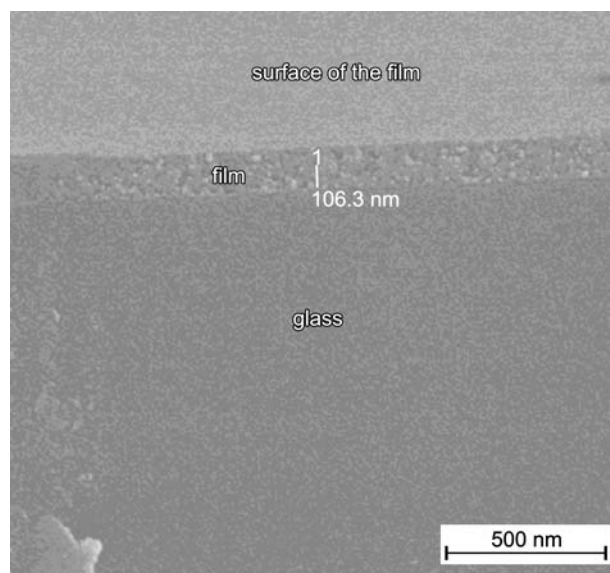


Figure 2. Surface and thickness of TiO₂ layer prepared by two subsequent depositions of a film on the slide glass (heating temperature 550°C, time 1 h).

The layer consisting of one film is not smooth and many aggregates were found on its surface. The layer consisting of two films yielded totally smooth surface, while the surface of the three films layer appears to be wrinkled.

The intensity of the light colour shade of the sample covered by the layer depends on the film thickness and on the angle of light incidence. The colour shade varies from yellow to violet according to the angle of incidence and became brighter and more intensive with increasing number of films deposited. The variety of colour shade is probably caused by interference of light [27].

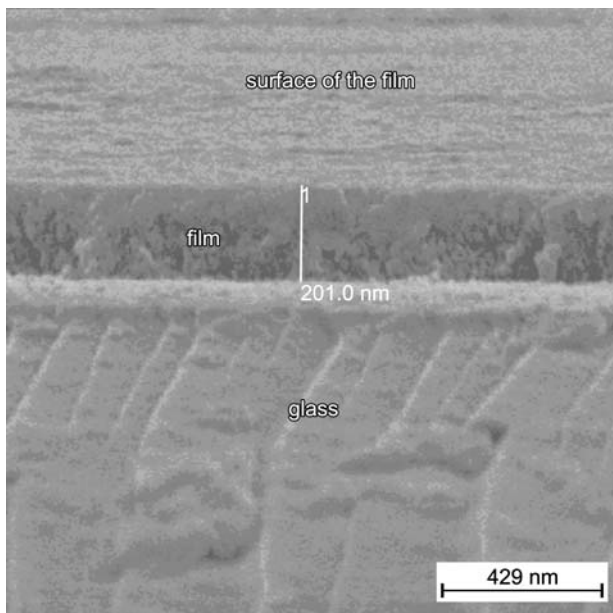


Figure 3. Surface and thickness of TiO₂ layer with three films on the slide glass (heating temperature 550°C, time 1 h).

Optical absorbance

The figure 4 shows that optical absorbance in UV-region increases with increasing number of coatings. The absorption edge of the TiO₂ film prepared by 1 coating cycle is observed at a shorter wavelength range than that of the TiO₂ films prepared by 2 and 3 cycles. The shift is ascribed to the difference in crystallite size. According to Young Ug Ahn et al. [1] the TiO₂ thin films prepared at 400 and 600°C have high transparency in the visible range of light. The band fluctuation is due to the interference colour of the film that appeared in the wavelength range of 400-900 nm.

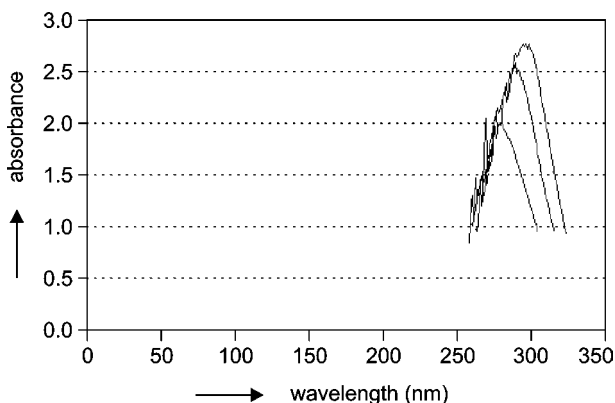


Figure 4. Absorbance of TiO₂ layers with 1, 2 and 3 films on the slide glass (550°C, 1 h).

Results of corrosion tests

The time dependence of the Na⁺ concentration extracted into corrosion solution from samples coated by one TiO₂ film was found to have a little distinctive parabolic shape, which can be approximated by a linear dependence except the first time values. The TiO₂ films proved a small protective effect against demineralised water (see figure 5). Van Gestel et al. [28] investigated the corrosion of micro and mesoporous Al₂O₃, Al₂O₃-TiO₂ and TiO₂ membrane materials in acid and alkaline solutions. They emphasized in accordance with previous works [29, 30] the importance of material parameters like the phase structure and the presence of amorphous phases. The resistance of TiO₂ layers on glass will be given especially by the strength of Si-O-Na and probably also Ti-O-Na bounds. According the results of RTG analysis, incorporation of TiO₂ into glass structure is not completed and TiO₂ is present also as anatase. In such a case the materials parameters mentioned above can also play an important role in the resulting corrosion resistance.

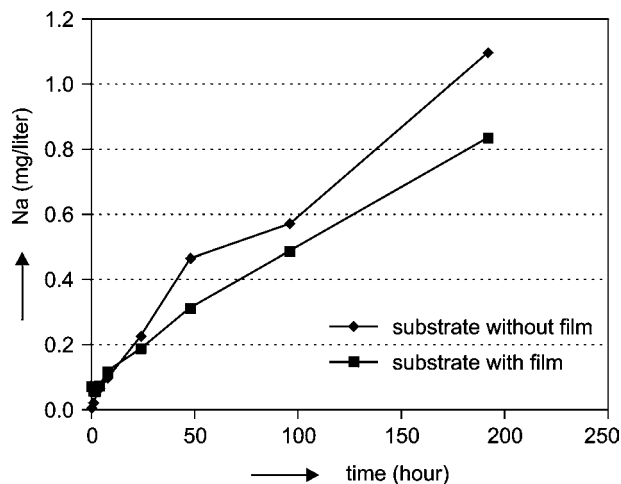


Figure 5. The time dependence of Na⁺ concentration in demineralised water after corrosion of the sample with one TiO₂ film at 80°C.

Porosity

The porosity of the thin films *P* was calculated using the following equation [31]:

$$P = \left(1 - \frac{n^2 - 1}{n_d^2 - 1} \right) 100 (\%)$$

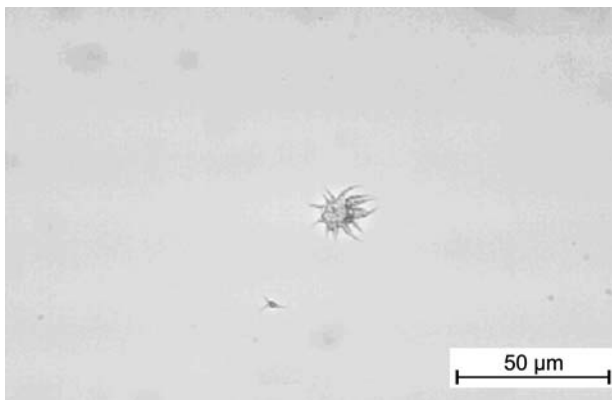
where *n_d* is the refractive index of pore-free anatase (*n_d* = 2.52) [32], and *n* is the refractive index of the porous thin films. The porosity value varied from 55 % (one film) to 59 % (layer consisting of three films). The resultant refractive index and porosity of TiO₂ thin films

prepared by heating at 550° C are 1.84 and 55% respectively. Seung Hun Oh et al. [33] reported a refractive index of 1.93 and porosity of 49.1% for layers prepared at 500° C. The porosity value obtained in this work seems to be high due to some uncertainties by measurement of refractive index of thin layers.

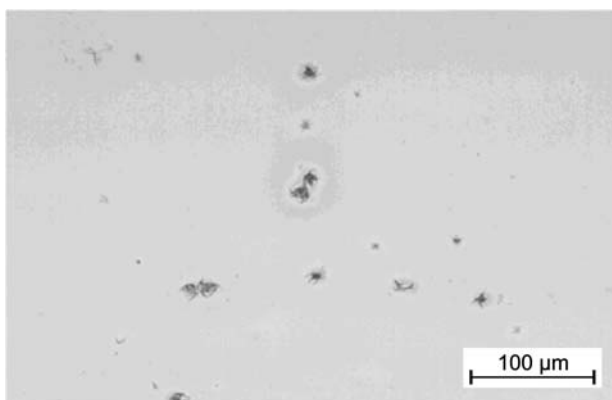
Optical microscopy

The figure 6 shows pictures of TiO₂ layers prepared at different conditions (temperature and different number of films deposited) obtained by optical microscope using the image analysis method of the system LUCIA.

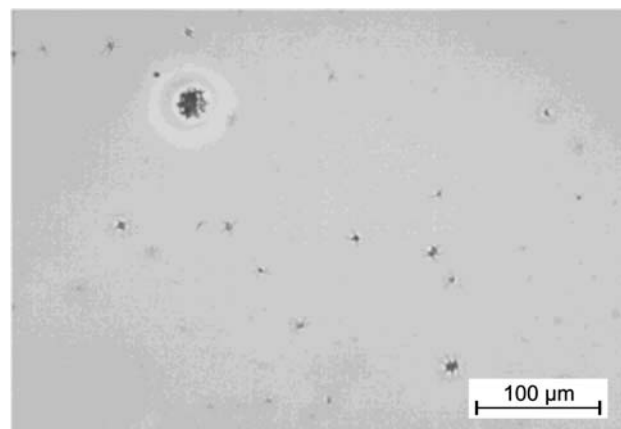
The figure 6a shows TiO₂ film prepared by temperature treatment at 350°C for 1 h. The figures 6b and 6c show TiO₂ layers prepared by temperature treatment at 550°C for 1 h consisting of two and three films. The particles observed were identified as anatase crystals with the size of 10 - 50 μm. The figures 6b and 6c indicate that the coating number of the TiO₂ film does not affect the particle size. This is in agreement with the work of Shang et al. [36] who found that the thickness of the TiO₂ film does not affect the particle size at least up to the thickness of 360 nm.



a)



b)



c)

Figure 6. TiO₂ films prepared by different temperatures and by different number of coatings. a) 350°C, 1 h, one coating; b) 550°C, 1 h, two coatings; c) 550°C, 1 h, three coatings.

RTG analysis

Figure 8 illustrate the XRD patterns of TiO₂ layers prepared at different temperatures for different hours on the surface of silica glass. The XRD data indicate that films are amorphous if only one or two films were deposited and submitted to heat treatment at 600°C for 8 hours. Amorphous phase was identified also in the layer prepared by deposition of one film and treated by temperature of 700°C for 8 h. The TiO₂ layer prepared by subsequent deposition of three films and/or treated by higher temperature contains nanocrystalline anatase.

Figure 7 show an influence of temperature, time of temperature treatment and number of coatings on crystallization of anatase (intensities of peaks). Crystalline TiO₂ film exists in three phases: anatase (tetragonal), rutile (tetragonal), and brookite (ortho-rhombic), rutile being the most stable of the three. The formation of the phases depends on starting material, deposition method and temperature. TiO₂ thin films can be transformed from amorphous phase into crystalline anatase and from anatase into rutile by temperature treatment [34]. The intensities of the anatase peaks were increased implying an improvement in crystallinity due to the increment of the films number. As the films number increases, the TiO₂ crystallites continue to grow. Similar effect exhibits also increased temperature of thermal treatment of the layer.

The results presented here agree with the conclusions of the work published previously [25]. In this work a negligible influence of solvent on the absorbance spectra of the films was found. For this reason, only ethanol was used as a solvent for sol preparation. It was confirmed, that the gels annealed at temperatures up to 350°C are amorphous, while at higher temperatures anatase diffraction peaks were found in gels annealed.

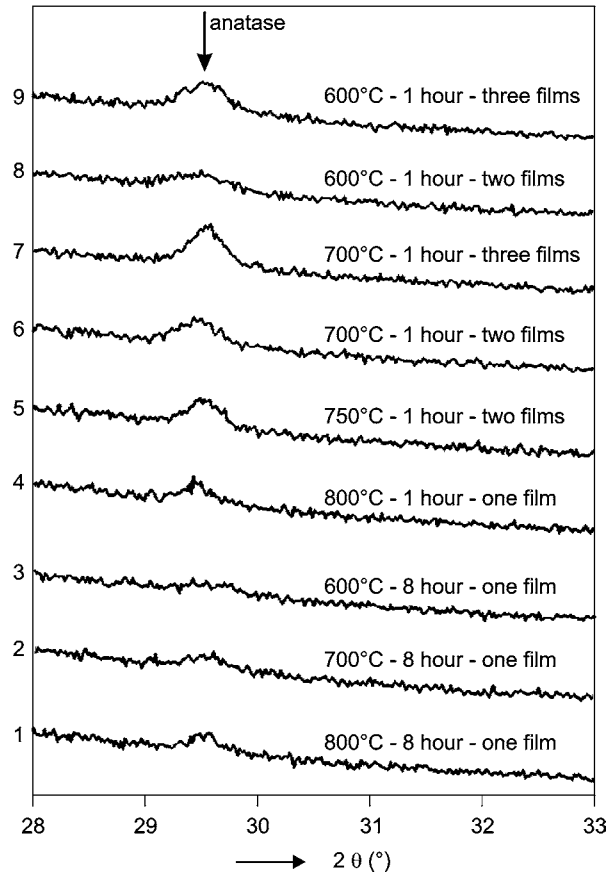


Figure 7. XRD patterns of TiO₂ films prepared by heating at different temperatures, heating times and with different films number.

In both works, the anatase to rutile phase transformation was not detected. It was observed in previous and also in the present work that the titania films on glass are transparent in visible region and show absorption in UV region. The layers were prepared by means of dip coating method in both works using the same drawing velocity and under atmospheric pressure and normal air humidity. The films with one coating showed characteristic absorption in UV region at a wavelength of around 280 nm in both works.

CONCLUSIONS

The TiO₂ films obtained using of tetra-n-butyl orthotitanate as the precursor and dip-coating method as the way of formation were homogeneous with good adhesion to the glass substrate and had small protective effect against demineralised water. The thickness of the layers increased with the number of coatings and varied from 88 nm (one coating) to 201 nm (three coatings). The highest values of optical absorbance of the layers were found to be in UV region between the wavelengths of 280 and 300 nm. The absorbance of TiO₂ layers increased with increasing number of films deposited

and decreased with temperature of layers preparation. The intensities of the anatase peaks in RTG diagrams increased with the number of films deposited and with the temperature used for preparation of the layer.

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References

1. Young U., Eui J., Hwan T., Sung H.: *Materials Letters* 57, 4660 (2003).
2. Jing S., Wei L., Yongfa Z.: *Journal of Molecular Catalysis A: Chemical* 202, 187 (2003).
3. Yu J., Zhao X., Zhang G., Han J., Zhao Q.: *Materials Science* 1, 16 (2001).
4. Andriainarivelo M., Corriu R., Mutin P., Vioux A.: *Chem. Mater.* 9, 1098 (1997).
5. Dislich H., Hussmann E.: *Thin Solid Films* 77, 129 (1981).
6. Makishima A., Asami M., Wada K.: *J. Non-Cryst. Solids* 121, 310 (1990).
7. Baudry P., Rodrigues A., Aegerter M.: *J. Non-Cryst. Solids* 121, 319 (1990).
8. Orel B., Macek M., Surca A.: *Proc. SPIE* 2255, 273 (1994).
9. Orel B., Lavrencic U., Hutchins M., Kalcher K.: *J. Non-Cryst. Solids* 175, 251 (1994).
10. Hagfeldt A., Vlachopoulos N., Gilbert S., Gratzel M.: *Proc. SPIE* 2255, 297 (1994).
11. Stromme M., Gutarra A., Niclasson G., Granqvist C.: *J. Appl. Phys.* 79, 3749 (1996).
12. Bell J., Barczynska J., Evans L., McDonald K.: *Proc. SPIE* 2255, 324 (1994).
13. Schroeder H.: *Physics of Thin Films* 5, 123 (1969).
14. Yoldaz B.: *US Patent* 4 361 598 (1982).
15. Yoldaz B., O'Keefe T.: *Appl. Opt.* 23, 3638 (1984).
16. Thomas I.: *Appl. Opt.* 26, 4688 (1987).
17. Biswas P., Kundu D., Ganguli D.: *J. Mater. Sci. Lett.* 8, 1436 (1989).
18. Floch H., Priotton J.: *Thin Solid Films* 175, 173 (1989).
19. Brinker C., Harrington M.: *Sol. Energy Mater.* 5, 159 (1981).
20. Atta A., Biswas P., Ganguli D.: *J. Mater. Sci. Lett.* 12, 760 (1993).
21. Nishide T., Shinoda M.: *Thin Solid Films* 238, 163 (1994).

22. O'Regan B., Moser J., Anderson M.: *J. Phys. Chem.* *94*, 8720 (1990).
23. Pulker H., Paesold g., Ritter E.: *Appl. Opt.* *15*, 2986 (1976).
24. Matthews D., Infelta P., Gratzel M.: *Sol. Energy Mater. Sol. Cells* *44*, 119 (1996).
25. Rodriguez L., Matoušek J.: *Ceramics-Silikáty* *47*, 28 (2003).
26. Chul Han Kwon at all: *Ceramics International* *29*, 851 (2003)
27. T. Yoko, K. Kamiya, S. Sakka.: *J. Ceram. Soc. Jap.* *95*, 150 (1987).
28. Van Gestel T., Vandecasteele C., Buekenhoudt A., Dotremont C., Luyten J., Leysen R., Van der Bruggen B., Maes G.: *Journal of Membrane Science* *207*, 73 (2002).
29. Holstein T., Corrosion of advanced ceramics by liquid media: a review in: *Proceedings of the Ninth CIMTEC-World Ceramic Congress*, pp. 433-444, Florence, Italy, 14-19 June 1999..
30. Westerheide R., Holstein T., Futing M., Aqueous corrosion of advanced ceramics, in: *Proceedings of the Euromat 1999*, pp. 392-397, Munich, Germany, 27-30 September 1999.
31. Yoldas B.E., Partlow P.W.: *Thin Solid Films* *129*, 1 (1985).
32. Kingery W.D., Bowen H.K., Uhlmann D.R.: *Introduction to Ceramics*, Wiley, NY, (1976).
33. Seung H., Dong J., Sung H., Eui J.: *Materials Letters* *57*, 4151 (2003).
34. Kim D., Hahn S., Oh S., Kim E.: *Materials Letters* *57*, 355 (2002).
35. Krejčová Z., Mecner P., Strnad Z., Hollerová I., Pech P.: *Sklář a keramik* *52*, 81 (2002).
36. Shang J., Li W., Zhu Y.: *Journal of Molecular Catalysis A: Chemical* *202*, 187 (2003).

VLASTNOSTI TiO₂ SOL-GEL VRSTEV
NA SKELNÉM SUBSTRÁTU

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TiO₂ tenké vrstvy byly připraveny s použitím procesu sol-gel a techniky dip-coating. Roztok pro nanášení vrstvy byl připraven s použitím tetra-n-butyl orthotitanátu (C₁₆H₃₆O₄Ti) jako prekursoru. S použitím tohoto alkoxydu v přítomnosti kyseliny octové a acetylacetonu jako chelátového činidla byly připraveny velmi stabilní soly tohoto oxidu. Získané vrstvy byly transparentní s dobrou adhezí k substrátu ze sodno-vápenatého skla. Byla zjištěna závislost optické absorbance a tloušťky vrstev na počtu na sobě nanesených vrstev a mikrostruktura povrchu vrstev byla zkoumána s použitím SEM. Absorpční spektra vykazovala zvýšenou absorbanci vrstev v oblasti 280-300 nm. U filmů připravených za vyšších teplot byly detekovány nanokrystalické částice ananasu. Tloušťka vrstev kolísala od 80 do 200 nm v závislosti na počtu nanesených filmů. Koróze substrátu pokrytého vrstvou byla sledována za použití demineralizované vody a bylo zjištěno, že je poněkud nižší ve srovnání s původním nepokrytým povrchem skelného substrátu.