

STUDY OF ANNEALING TEMPERATURE VARIATION ON THE STRUCTURAL PROPERTIES OF DIP-COATED TiO₂-SiO₂ NANOSTRUCTURED FILMS

M. Alzamani^{1,*}, A. Shokuhfar¹, E. Eghdam¹ and S. Mastali²

* mehdi_zamani1361@yahoo.com

Received: December 2012

Accepted: February 2013

¹ Mechanical Department (Advanced Materials and Nanotechnology Research Lab), K. N. Toosi University of Technology, Tehran, Iran.

² Faculty of Metallurgical and Materials Engineering, Semnan University, Semnan, Iran.

Abstract: In the present research, SiO₂-TiO₂ nanostructure films were successfully prepared on windshields using the sol-gel technique for photocatalytic applications. To prevent the thermal diffusion of the sodium ions from the glass to TiO₂ films, the SiO₂ layer was pre-coated on the glass by the sol-gel method. The substrates were dipped in the sol and withdrawn with the speed of 6cm/min-1 to make a gel coating film. The coated films were dried for 2 days at 27 °C to allow slow solvent evaporation and condensation reactions due to rapid sol-gel reaction of Titania precursor. Then, the films were annealed at 100 °C for 30min and at the final temperature (500, 700 °C) for 30 min continuously. The structure and surface morphology properties, which are as a function of annealing temperature, have been studied by SEM; FE-SEM and XRD. The FE-SEM surface morphology results indicate that the particle size increases from 19 to 42 nm by increasing the annealing temperature from 500 °C to 700 °C. Likewise, XRD illustrate the crystal anatase and rutile as main phases for TiO₂-SiO₂ films annealed at 500 °C and 700 °C respectively. This procedure resulted in transparent, crack-free SiO₂-TiO₂ films.

Keywords: SiO₂-TiO₂, thin films, sol-gel, dip coating

1. INTRODUCTION

The development of automotive industries has always been paced by the results of research and development in the concurrent fields of design and materials technology. Production quality increase such as using self-cleaning glasses in windshields and catalysts to reduce pollutants, etc, have led to more efficient and commodious manufacturing, and surface engineering is now a key materials technology in the design of future advanced automotive industries. Hereto, researches tend to use TiO₂ thin films for windshields and lateral mirrors to improve their practical properties

Since the past decades, an increasing interest has been devoted to the study of titanium dioxide (TiO₂) thin films. Transparent TiO₂-SiO₂ films on glass could form the basis for self-cleaning of indoor windows, lamps or windshields. TiO₂ thin films have attracted considerable attention of use such as desensitized solar cells¹, photocatalysts [2,3], photoelectrodes¹, electro-chromic displays [4], waveguides [5], gas sensors [6], resonators [7], and biomaterials [8] due to its high activity, photochemical inertness, non-toxicity, efficiency, and low cost.

Titanium dioxide occurs in three different crystalline Polymorphic forms: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Among these, the anatase phase usually exhibits the best photocatalytic behavior, while the rutile phase is the most stable phase. Photocatalysts may be used as a suspension in an aqueous solution or it may be immobilized on to a supporting substrate. The immobilization method is more convenient for practical use since the main problem in the usage of TiO₂ suspended in an aqueous solution is the separation of TiO₂ nanoparticles after the photocatalytic reaction.[9] The lower amount of the rutile phase of TiO₂, the higher amount of the anatase phase of TiO₂ and the better photocatalytic activity [10-12].

A variety of techniques have been used for the preparation of TiO₂ films including chemical vapor deposition [13,14], Sol-gel [2-4,15], sputtering [6,16] and electron-beam evaporation (EBE) [17,18]. TiO₂ film properties strongly depend on their microstructure that should be strictly controlled in order to obtain a tailored performance.

Among all the possible techniques existing to elaborate TiO₂ films, the sol-gel process is now

widely used [19]. The sol–gel coating method is one of the promising methods because the microstructure of the film is easily controlled with changing the solution composition and deposition condition. In addition, it provides uniform porous TiO₂ films with large specific surface area, which is favorable in achieving good photoactivity [20].

This method allows the modification of the structure and the microstructure of the deposited titanium oxide playing on the sol composition, the coating parameters and the thermal treatment conditions. Furthermore, the sol–gel process does not necessitate the use of expensive equipments as it is the case for vacuum deposition techniques [21].

The properties of the sol–gel TiO₂ thin films are highly dependent on the structure (amorphous or crystallized), the thickness and the density of the deposited layers. These features are then mainly influenced by the sol composition, the sol viscosity, the withdrawal speed when the dip coating process is used, the substrate nature and the sintering mode [22,23].

The purpose of the present study is to experimentally assess the TiO₂-SiO₂ films for advanced windshields for use in self-cleaning applications. Specifically, annealing temperature as the key feature of the layer which affect performance, microstructure and the fundamental phase that must be considered, are addressed.

2. EXPERIMENTAL METHOD

2. 1. Materials

Titanium tetra isopropoxide (TTIP, 99 %, PANRIC) and Tetraethyl ortosilicate (TEOS, 98%, ACROS) were used as precursors. 2-propanol (99.7%, MERCK) and ethanol (96%, MRECK) served as solvents; hydrochloric acid (HCL, 37%, MERCK) was used as a catalyst. diethanolamine (DEA, 99.5%, MERCK) was used as stabilizing agent and a modulator was added into the TiO₂ sols.

2. 2. Preparation of Sols

The preparation procedure for making silica sol is similar to that reported in former publication [24]. TiO₂ thin films were prepared

by the sol–gel dip coating technique, which is based on the hydrolysis of alkoxides in alcoholic solutions. In this study, DEA with DEA/TTIP molar ratio of 1:1 was employed. The procedure of preparation includes the dissolution of the mixture of 1:25 moles of 2-propanol as solvent and TTIP as precursor with the mixture of 1:1 mole of DEA and distilled water. A flow chart of this method is presented in Fig. 1.

2. 3. Preparation of Samples

The windshield glasses were used as the substrates. The specimens in the form of slides with dimension of 100×20×2mm were used as the substrate to support the TiO₂-SiO₂ films. At first, substrates were cleaned in an ultrasonic cleaner full of de-ionized water, then in ultrasonic cleaner with acetone. Subsequently specimens were heated at the temperature of 60 °C for 1h and immediately coated.

2. 4. Dip Coating

The substrates were dipped in the sol and withdrawn at a speed of 1cm/min⁻¹ to make a gel coating film. The coated films were dried for 2 days at 27 °C to allow slow solvent evaporation and condensation reactions due to rapid sol–gel reaction of Titania precursor. Then the samples were heated. The furnace temperature increased at heat rate of 10 °C min⁻¹ until 100 °C; this temperature was held for 30 min. The coated substrates were dried at 100 °C for 30 min to improve the adhesion of films on glasses and to release residual stresses. The temperature of the furnace was subsequently increased at heat rate of 10 °C min⁻¹ to the final temperature (500 °C and 700 °C) and held at this temperature for 30 min to accomplish the crystallization of gel films. Finally, the films were cooled in the furnace to room temperature.

2. 5. Characterization of TiO₂ Films

The main phase present was identified and the crystal size of the TiO₂-SiO₂ thin films was determined by an X-ray diffractometer (XRD) (D8 Advance, Bruker Co., Germany) using

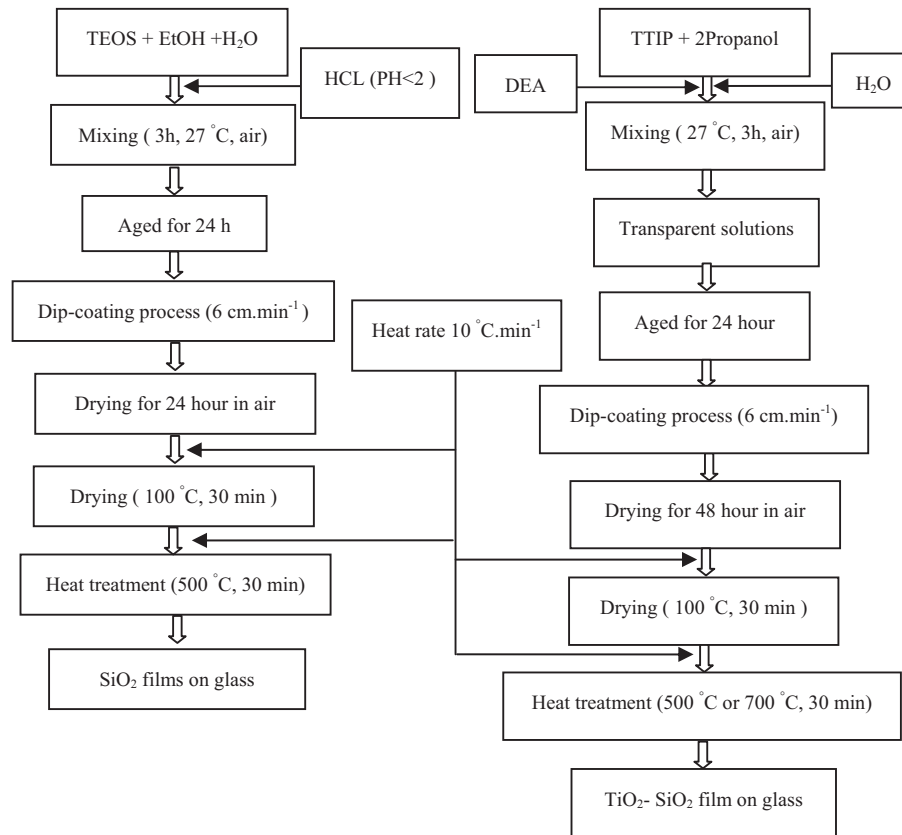


Fig. 1. Experimental procedure used in this research (left: preparation process of SiO₂ films, right: the preparation process of TiO₂-SiO₂ films).

monochromatic Cu-K α radiation operated at 40 kV and 30 mA at a scan speed of 0.02 sec per step with an increment of 0.02 ° per step. The crystal size was calculated from X-ray line broadening analysis by Scherrer formula. Film morphology was characterized by scanning electron microscopy (SEM; Tescan model Vega-II) and field-emission-scanning electrons microscopy (FE-SEM, S-4160).

3. RESULTS AND DISCUSSION

3. 1. Surface Morphology of TiO₂-SiO₂ Films

The surface morphology of TiO₂-SiO₂ films were examined using SEM. Fig. 2 shows SEM micrographs of TiO₂-SiO₂ films on substrate annealed at (A) 500 °C and (B) 700°C for 30 min in air. Temperature increasing may lead to non-uniform and cracked coating and reduce coating lucidity and transparency (As can be seen in Fig. 2). This is due

to substrate plasticity and softening at temperature of 700 °C.

Fig. 3 shows FE-SEM images of TiO₂-SiO₂ films prepared at 500 °C and 700 °C at two magnifications of 100,000 and 150,000. The FE-SEM images revealed that the surface morphology of the TiO₂-SiO₂ films depend strongly upon annealing temperature. It was observed that the average grain size of the films increases significantly when annealing temperature increases.

At low temperatures (Fig. 3.A and C) many nucleation centers are present on the substrate and small crystals are produced. Then, the films with small crystal size are not able to grow into bigger ones. Whereas for higher annealing temperatures (Fig. 3.B and D), the film crystal sizes become larger. In fact, for the samples annealed from 500 °C to 700 °C, the FE-SEM shows an increase in the crystal size from 19 nm to 42 nm. This increase is due to the anatase-to-rutile phase transformation, which is observed in XRD results.

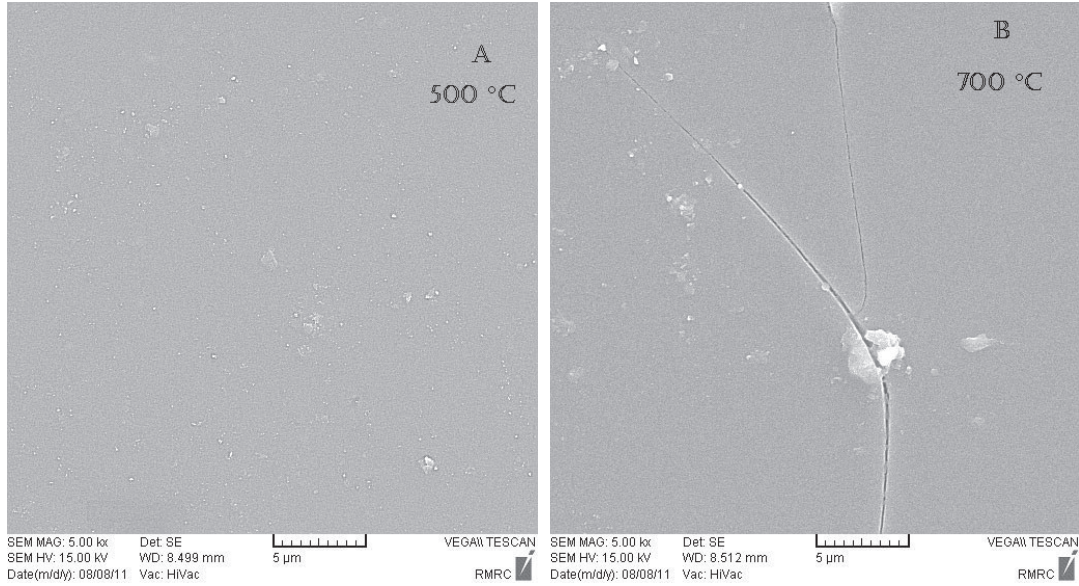


Fig. 2. SEM micrographs of $\text{TiO}_2 - \text{SiO}_2$ films prepared in annealing temperature (A) 500 °C (B) 700 °C

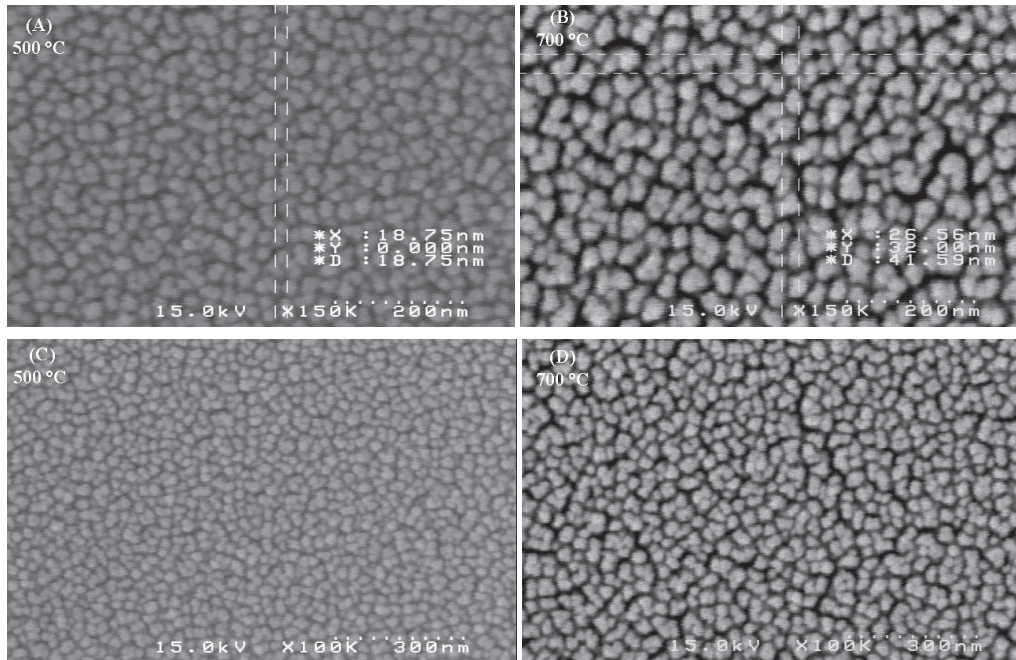


Fig. 3. FE-SEM micrograph of a $\text{TiO}_2 - \text{SiO}_2$ films annealed at (A,C) 500 °C, (B,D) 700 °C.

3. 2. Crystal Structure of $\text{TiO}_2 - \text{SiO}_2$ Films

In order to compare the crystal composition and crystal size of the films prepared at different annealing temperatures (500, 700 °C), XRD test

was employed. Fig. 4 (a & b) presents the results of XRD analysis for $\text{TiO}_2 - \text{SiO}_2$ films.

The XRD pattern (Fig. 4.a) clearly shows that the main peak of films annealed at 500 °C is at 25.48, which corresponds to anatase (101) plane.

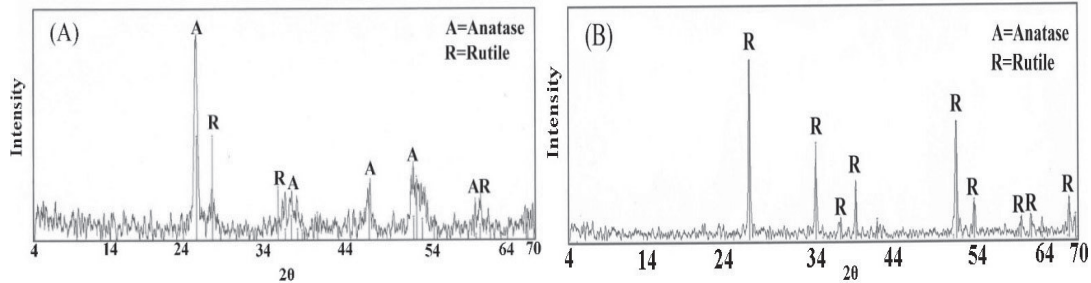


Fig. 4. XRD patterns of $\text{TiO}_2\text{-SiO}_2$ films produced on glass Substrates annealed at (A) 500 °C and (B) 700°C for 30 min in air.

Fig. 4.b represents that the main peak of Films annealed at 700 °C is at 27.42, which corresponds to rutile (110) plane. The peak corresponding to rutile phase (rutile TiO_2 in the (110) plane) can be clearly seen in the films annealed at 700 °C which has high intensity compared to prior sample. Relatively low annealing temperatures (for instance, 500 °C) cannot lead to anatase-to-rutile crystal phase transformation. High annealing temperatures (for instance, 700 °C) lead to the transformation of anatase to rutile. One can deduce from Ref. 25 that the anatase to rutile phase transformation take place at temperatures from 600 to 700 °C. There is a decrease of anatase phase (101) for $\text{TiO}_2\text{-SiO}_2$ films after increasing annealing temperature from 500 to 700 °C.

The XRD results of the $\text{TiO}_2\text{-SiO}_2$ films in annealing temperature of 500 °C showed a phase distribution of 91:9 anatase:rutile, with crystal size of 16 and 38 nm, for anatase and rutile, respectively. Also XRD results of the $\text{TiO}_2\text{-SiO}_2$ films in annealing temperature of 700 °C showed a phase distribution of 6:94 of the phase anatase:rutile, with crystal size of 22 nm (anatase) and 42 nm (rutile) across. The crystal size of the $\text{TiO}_2\text{-SiO}_2$ films in annealing temperature of 500 °C is calculated using the Scherrer's equation based on the full peak width at half maximum intensity (FWHM) of anatase phase (101).

The FWHM of anatase phase (101) in $\text{TiO}_2\text{-SiO}_2$ films is at the average crystal size of 16-22 nm. Otherwise, results on average crystal size of the $\text{TiO}_2\text{-SiO}_2$ films in annealing temperature 700 °C calculated using the

Scherrer's equation based on the FWHM of rutile phase (110) derived from XRD patterns revealed rutile as the main crystal phase, with a fundamental crystal size of 38–42 nm.

4. CONCLUSIONS

This work presents the annealing temperature effect on the microstructure and morphologic properties of $\text{TiO}_2\text{-SiO}_2$ film. This research proved that annealing temperature is an important parameter to affect the structure; surface morphology and photocatalytic activity of the $\text{TiO}_2\text{-SiO}_2$ films.

1. $\text{TiO}_2\text{-SiO}_2$ coating attained by sol-gel dip coating technique was uniformly and crack-free. The coatings thickness was desirable and in the range of nanofilms.
2. Increasing of annealing temperature of the $\text{TiO}_2\text{-SiO}_2$ films, resulted in the changes of the film surface morphology and microstructure, and affected the ratio of anatase–rutile crystal phases and the photocatalytic activity of TiO_2 .
3. XRD shows the crystal anatase and rutile as main phases for $\text{TiO}_2\text{-SiO}_2$ films annealed at 500 °C and 700 °C, respectively. Coatings annealed at temperatures below 100 °C are not adhesive, do not adhere well to the windshields substrate, and flake off into the solution. Annealing at 200 °C gives a film that can be removed from the glass substrate by soft scratching. Films annealed at 500 °C are adherent. Annealing at 700 °C for automotive glass substrate is not suitable and practical, because at this

temperature glass substrate begins to soften and lucidity reduced.

4. The FE-SEM surface morphology results indicate that the particle size increases from 19 to 42 nm by increasing the annealing temperature from 500 °C to 700 °C.

It was anticipated that too low temperatures would not eliminate the organic residues while too high temperatures could induce the transformation from anatase to rutile, which is in principle undesired for functional applications of the TiO₂-SiO₂ coatings.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support of the SAPCO CO. (SUPPLYING AUTMOTIVE PARTS CO.).

REFERENCES

1. O'Regan, B., Gratzel, M., *Nature.*, 1991, 353, 737.
2. Barzegar, B., Ashrafi zadeh, S. N., Ashrafi zadeh, F., "Preparation of Catalytic Coating of Titanium Oxide by Means of Electrolytic Deposition", *Iranian Journal of Materials science and Engineering*, 2004, 1, 9-15.
3. Yu, J., et al. "Preparation, Microstructure and Photocatalytic Activity of the Porous TiO₂ Anatase Coating by Sol-Gel Processing", *Journal of Sol-Gel Science and Technology*, 2000, 17, 163-171.
4. Nagase, K., et al, "Preparation of Vanadium-Titanium Oxide Thin Films by Sol-Gel Method and Their Electro-chromic Properties", *Journal of Ceramic Society of Japan*, 1993, 101, 1032-1037.
5. Sorek, Y., et al, "Sol-gel glass waveguides prepared at low temperature", *Applied Physics Letters*, 1993, 63, 3256-3259.
6. Tang, H., et al, "TiO₂ anatase thin films as gas sensors", *Sensors and Actuators B*, 1995, 26, 71-75.
7. Kersale, Y., et al, "Cryogenic monolithic sapphire-rutile temperature compensated resonator oscillator", *IEEE Transaction on Ultrasonic Ferroelectrics and Frequently Control*, 2003, 50, 1662-1666.
8. Kommireddy, D. S., Sriram, Sh. M., et al, "Stem cell attachment to layer-by-layer assembled TiO₂ nanoparticle thin films", *Biomaterials*, 2006, 27, 4296-4303.
9. Segota, S., Curkovic, L., Ljubas, D., et al., "Synthesis, characterization and photocatalytic properties of sol-gel TiO₂ films", *Ceramics International*, 2011, 37, 1153-1160.
10. Chen, J., Poon, C., "Photocatalytic construction and building materials: From fundamentals to applications", *Building and Environment*, 2009, 44, 1899-1906.
11. Carp, O., Huisman, C. L., Reller, A., "Photoinduced reactivity of titanium dioxide", *Progress in Solid State Chemistry*", 2004, 32, 33-177.
12. Fujishima, A., Zhang, X., Tryk, D. A., "TiO₂ photocatalysis and related surface phenomena", *Surface Science Reports*, 2008, 63, 515-582.
13. Ha, H. Y., "et al, Properties of the TiO₂ membranes prepared by CVD of titanium tetraisopropoxide", *Journal of Membrane Science*, 1996, 111, 81-92.
14. Hermann, G. S., "et al, X-ray photoelectron diffraction study of an anatase thin film: TiO₂ (001)", *Surface Science*, 2000, 447, 201-211.
15. Kajihara, K., Yao, T., "Macroporous Morphology of the Titania Films Prepared by a Sol-Gel Dip-Coating Method from the System Containing Poly(Ethylene Glycol). III. Effect of Chemical Additives", *Journal of Sol-Gel Science and Technology*, 2000, 16, 257-266.
16. Takeda, S., "et al, Photocatalytic TiO₂ thin film deposited onto glass by DC magnetron sputtering", *Thin Solid Films*, 2001, 392, 338-344.
17. Bhattacharyya, D., "et al, Spectroscopic ellipsometry of TiO₂ layers prepared by ion-assisted electron-beam evaporation", *Thin Solid Films*, 2000, 360, 96-102.
18. Wang, Y. L., Zhang, K. Y., "Study of the growth morphology of TiO₂ thin films by AFM and TEM", *Surface and Coatings Technology*, 2001, 140, 155-160.
19. Brinker, C. J., Scherer, G. W., "Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing", Academic Press Inc., San Diego, 1990.
20. Oh, S. H., "et al, Comparison of optical and

- photocatalytic properties of TiO₂ thin films prepared by electron-beam evaporation and sol-gel dip-coating, *Materials Letters*, 2003, 57, 4151-4155.
21. Vives, S., Meunier, C., "Densification of amorphous sol-gel TiO₂ films: An X-ray reflectometry study", *Thin Solid Films*, 2010, 518, 3748-3753.
 22. Brinker, C. J., Hurd, A. J., "Fundamentals of sol-gel dip-coating", *J. Phys. III France*, 1994, 4, 1231-1242.
 23. Scherer, G. W., "Sintering of sol-gel films", *Journal of Sol-Gel Science and Technology*, 1997, 8, 353-363.
 24. Endres, K., "et al, Enhancement of fracture strength of cutted plate glass by the application of SiO₂ sol-gel coatings", *Thin Solid Films*, 1999, 351, 132-136.
 25. Takahashi, Y., Matsuoka, Y., "Dip-coating of TiO₂ films using a sol derived from Ti(O-i-Pr)₄-diethanolamine-H₂O-i-PrOH system", *Journal of Materials Science*, 1988, 23, 2259-2266.