PROGRESS IN COLOR, COLORANTS AND COATINGS

available online @ www.pccc.icrc.ac.ir

Prog. Color Colorants Coat. 6(2013), 51-59

Ministry of Science, Research and Technology
Institute for Color Science and Technology

On the Investigation of Sol-Gel TiO_2 Nanostructured Films Applied on Windshields Pre-Coated with SiO_2 Layer by Dip-Coating Method

M. Alzamani[1], A. Shokuhfar[2], S. Mastali[3], E. Eghdam[4] and M. A. Hossaini[5*]

[1.] M.Sc., Mechanical Department, Advanced Materials and Nanotechnology Research Lab., K. N. Toosi University of Technology, P. O. Box: 19991-43344, Tehran, Iran.

[2.] Professor, Mechanical Department, Advanced Materials and Nanotechnology Research Lab., K.N. Toosi University of Technology, P. O. Box: 19991-43344, Tehran, Iran.

[3.] M. Sc., Faculty of Metallurgical and Materials Engineering, Semnan University, P. O. Box: 19111-35131, Semnan, Iran.

[4.] M. Sc., Mechanical Department, Advanced Materials and Nanotechnology Research Lab., K. N. Toosi University of Technology, P. O. Box: 19991-43344, Tehran, Iran.

[5.] Professor, chemistry & Environmental Department, SAPCO (Supplying Automotive Parts Co.), Tehran, Iran.

ARTICLE INFO

Article history:
Received: 22-09-2012
Final Revised: 12-11-2012
Accepted: 20-11-2012
Available online: 21-11-2012

Keywords:
SiO_2-TiO_2 film
Sol-gel
Surface morphology

ABSTRACT

TiO_2-SiO_2 photocatalytic nanostructure film on windshield was prepared via sol–gel dip-coating method for self-cleaning purposes. TiO_2 films were prepared on automotive glass pre-coated with a SiO_2 layer by a dip-coating method followed by annealing at 500 °C for 30 min. The films were characterized using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM, FE-SEM) techniques. The TiO_2-SiO_2 films were transparent, uniform and crack-free and the temperature was best chosen. XRD shows that SiO_2 pre-coated layer comparatively prevent rare elements ions diffusion from substrate to avoid unfavorable compounds. The results illustrate the crystalline anatase as main phase for films annealed at 500 °C with average crystallite size of 22-26 nm, which was preferable due to much higher photocatalytic activity of anatase compared to rutile phase. The FE-SEM surface morphology results indicate that the particle size was 22 nm, whereas some pores observed in the coatings which were due to un-perfect solvent evaporation. Prog. Color Colorants Coat. 6(2013), 51-59. © Institute for Color Science and Technology.

1. Introduction

By the 21st century and energy saving requirements in the automotive industries, self-cleaning glasses were advented so that, 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 improvements such as using self-cleaning glasses in windshields, catalysts to reduce pollutants, etc, have led

*Corresponding author: mahossaini@sapco.com

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 TiO_2 films as coating for windshields and lateral mirrors.

Since the past decades, an increasing interest has been devoted to the study of titanium dioxide (TiO_2) thin films. Transparent TiO_2-SiO_2 films on glass could form the basis for self-cleaning of indoor windows, lamps or windshields. TiO_2 thin films have attracted considerable attention of use such as desensitized solar cells [1], photo electrodes [1], photocatalysts [2-5], electro-chromic displays [6], waveguides [7], gas sensors [8], resonators [9], and biomaterials [10], due to its high activity, photochemical inertness, non-toxicity, efficiency, and low cost.

To maximize utilization of Titanium Dioxide for practical industrial applications, it is necessary to develop TiO_2 film type, especially for photocatalytic applications. Titanium Dioxide occurs in three different crystalline polymorphic forms: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) [11]. Among these, the anatase phase usually exhibits the best photocatalytic behaviour, 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 TiO_2 suspended in an aqueous solution is the separation of TiO_2 nanoparticles after the photocatalytic reaction [12]. Lower amount of the rutile phase of TiO_2 results in higher amount of the TiO_2 anatase phase, and so better photocatalytic activity [13-15].

A variety of techniques have been used for the preparation of TiO_2 films including chemical vapour deposition [16,17], sol–gel [2-6,18], sputtering [8,19] and electron-beam evaporation (EBE) [20,21]. TiO_2 film properties strongly depend on their microstructure that should be strictly controlled in order to obtain a tailored performance.

Among the techniques to elaborate TiO_2 films, the sol–gel process is now widely used [22]. The sol–gel method is the promising method, because the microstructure of the film is easily controlled with changing the solution composition and deposition condition. In addition, it provides uniform porous TiO_2 films with large specific surface area, which is favorable in photocatalytic activity [23]. This method allows the modification of the TiO_2 microstructure by variation in sol composition, the coating parameters and the thermal treatment conditions. Furthermore, the sol–gel process does not necessitate the use of expensive equipments as the case of vacuum deposition techniques [24]. The properties of the sol-gel TiO_2 films are highly dependent on the structure (amorphous or crystalline), the thickness and the density of the deposited layers. These features are then mainly affected by the sol composition and viscosity, the withdrawal speed when the dip-coating process is used, the substrate nature and the sintering mode [25, 26].

The objective of this paper is to experimentally assess the TiO_2-SiO_2 films for advanced windshields to use in self-cleaning applications. For this purpose, microstructure and the fundamental phase that must be considered are addressed.

2. Experimental

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%, Merck) served as solvents; hydrochloric acid (HCL, 37%, Merck) was used as catalyst. Diethanolamine (DEA, 99.5%, Merck) was used as stabilizing agent and a modulator was added into the TiO_2 sols.

2.2. Preparation of sols

The preparation procedure for making silica sol is similar to that reported in former publication [27]. TiO_2 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 preparation includes 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 Figure 1.

2.3. Preparation of samples

The automotive glasses were used as the substrates. The specimens in the form of slides with dimension of 100mm×20mm×2mm were used as the substrate to support the TiO_2-SiO_2 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 60 °C for 1 h and immediately coated.

2.4. Dip-coating

The substrates were dipped in the sol and withdrawn at a speed of 1 cm/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} to 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 500 °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 TiO_2 films

The main phase present was identified and the crystallite size of the TiO_2-SiO_2 thin films was determined by an X-ray diffractometer (XRD) (D8 Advance, Bruker Co., Germany) using monochromatic Cu–Kα 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 crystallite 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 Electron Microscopy (FE-SEM, S-4160).

3. Results and discussion

3. 1. Surface morphologies of TiO_2-SiO_2 films

The surface morphology of TiO_2-SiO_2 transparent thin films were examined using SEM and FE-SEM. Figure 2 shows SEM micrographs of TiO_2-SiO_2 films annealed at 500 °C for 30 min at furnace atmosphere at different magnification.

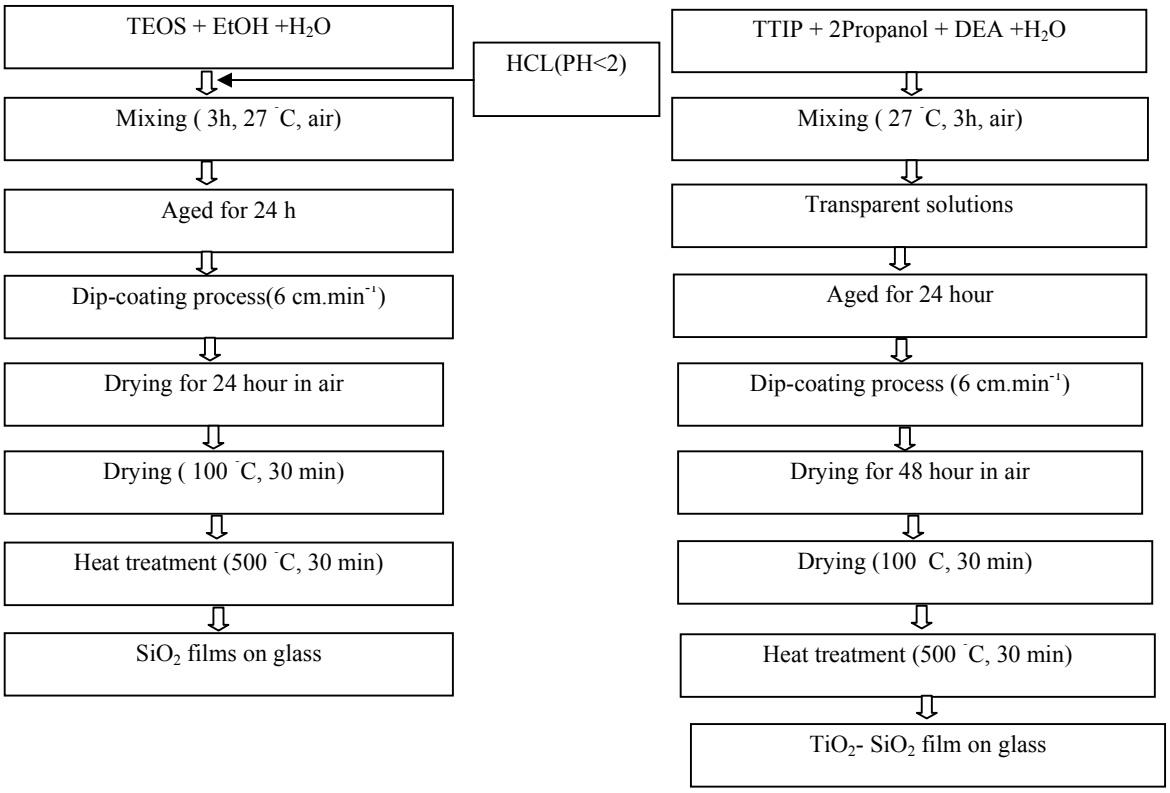

Figure 1: The flowchart of preparation method (left: preparation of SiO_2 films; right: the preparation of TiO_2-SiO_2 films).

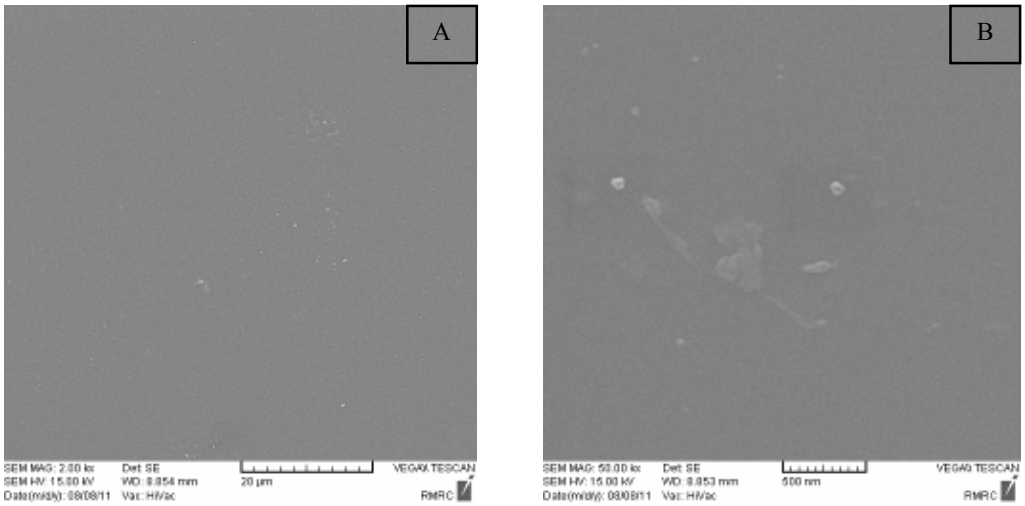

Figure 2: SEM graphs of films (different magnifications).

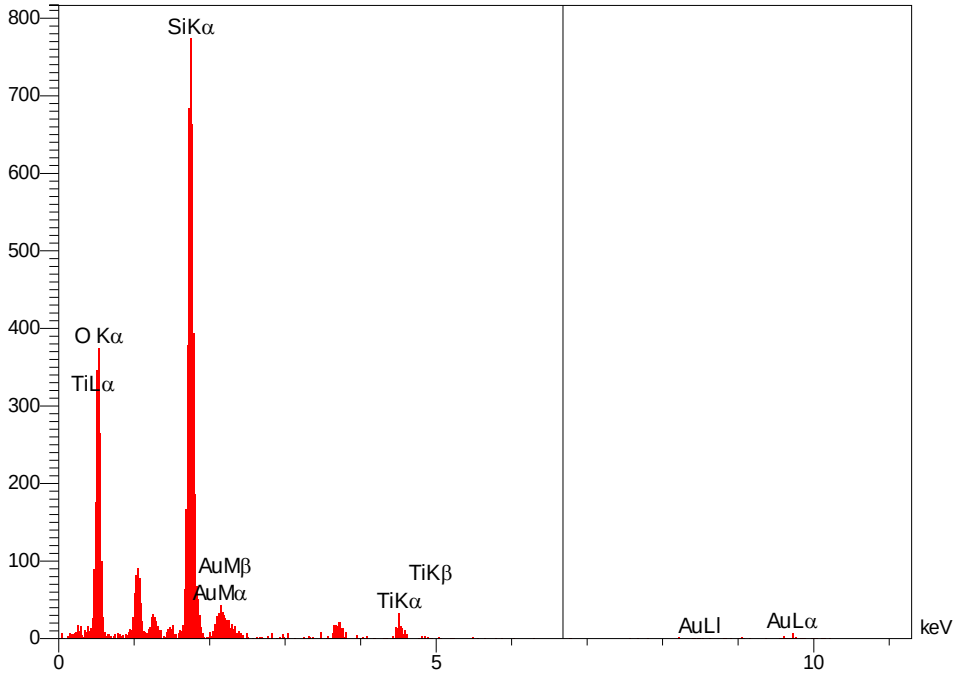

Figure 3: EDX analyses for the TiO_2 – SiO_2 film.

These porosities may improve the photocatalytic properties of the substrate. From the EDX analysis of the film (Figure 3), titanium was found to be one of the major components. Previous EDX analysis showed that the substrate glass have mainly been composed of silicon and oxygen. These elements react with Ti at the

annealing temperature to form compounds which decrease the photocatalytic property. So, in this research SiO_2 barrier layer have been pre-coated to prevent undesirable compounds. However, Small amounts of Na, Al, Au and K were also been found as impurities (Figure 3). By application of SiO_2 pre-coated layer via sol-gel process, the contents of these elements have been reduced compared to bare substrate. In addition to structural variations, these elements may decrease photocatalytic activity of TiO_2 nanostructured thin film.

The FE-SEM images revealed that the surface morphology of the TiO_2-SiO_2 films has appropriate distribution of TiO_2 particles without any agglomeration effects which can loss coating properties. Using image analysis, it was indicated that the average grain size of the particles in the coating was 22 nm (as can be seen in Figure 4). Figure 5 shows FE-SEM images of TiO_2-SiO_2 films prepared at 500 °C at four different magnifications to show the TiO_2 particles distribution. It can be considered that the particle distribution in the nanometric range is homogenous.

The thickness of the TiO_2-SiO_2 coating could be measured by the FE- SEM image from the cross section of the samples, Figure 6. The average thickness of the TiO_2-SiO_2 thin film was estimated to be 1 µm. According to this micrograph, one can deduce the columnar growth of the TiO_2 layer on the pre-coated of SiO_2.

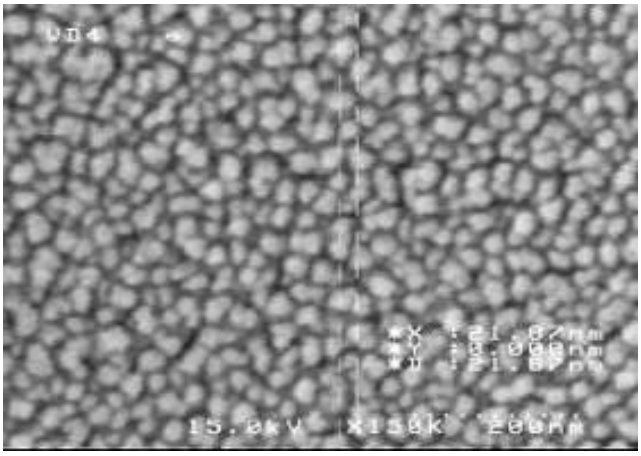

Figure 4: FE-SEM micrograph of the TiO_2 – SiO_2 coating showing TiO_2 particle size.

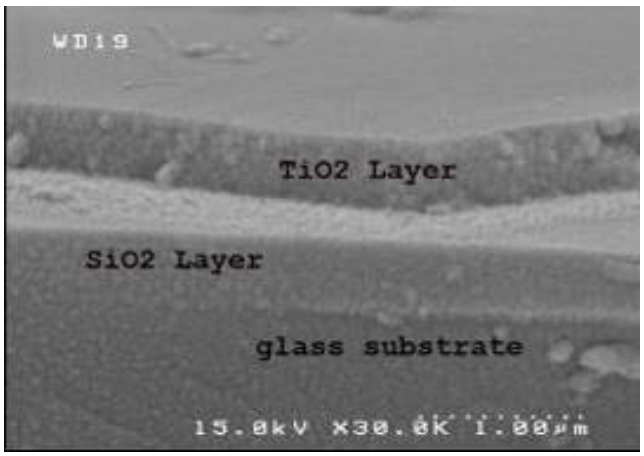

Figure 6: FE-SEM micrograph from the cross section of the TiO_2 – SiO_2 film on the glass substrate.

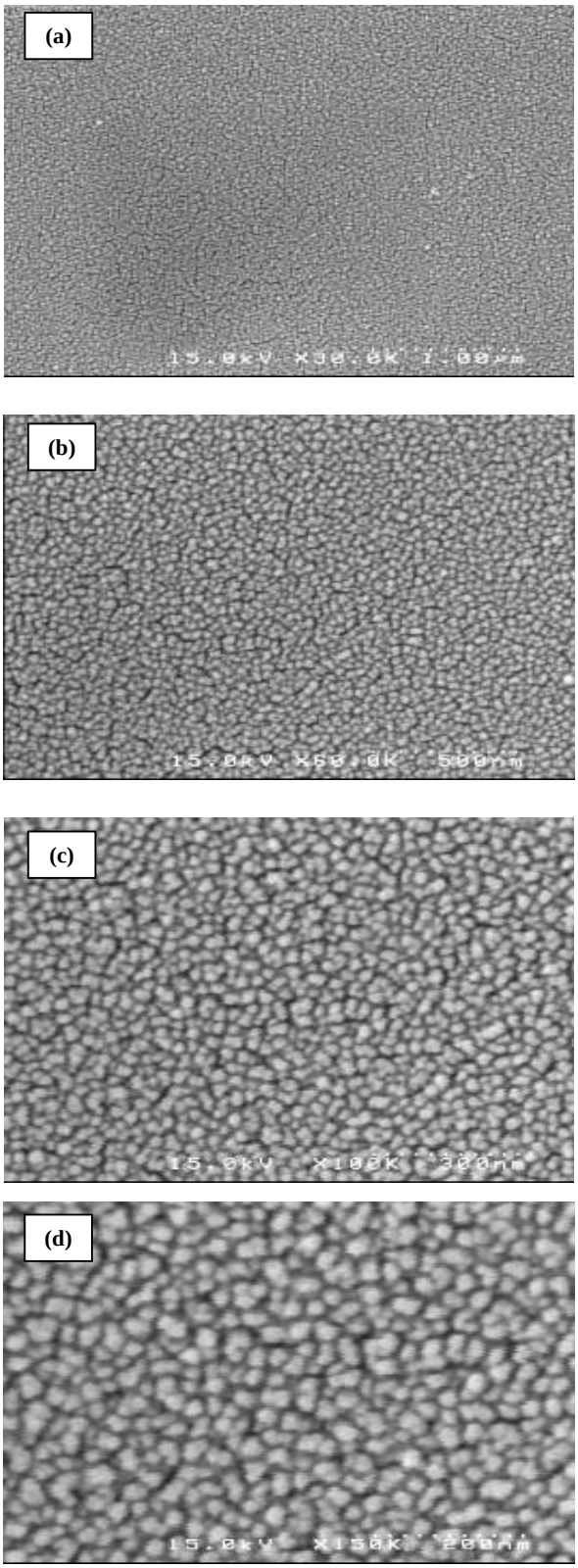

Figure 5: FE-SEM micrographs for the TiO_2 – SiO_2 film on glass at four magnifications of (a) 30000 X, (b) 60000 X, (c) 100000 X and (d) 150000 X.

3.2. Crystal structure of TiO_2-SiO_2 films

In order to investigate the composition and crystallite size of the coatings, X-ray Diffraction (XRD) experiments were employed. Figure 7 presents the results of XRD analysis for TiO_2-SiO_2 thin films.

The XRD pattern (Figure 7) clearly shows that the main peak of coatings annealed at 500 °C is at 25.48°, which corresponds to anatase (101) plane. Relatively low annealing temperatures (for instance, 500°C) cannot lead to anatase-to-rutile crystal phase transformation. One can deduce from Ref. 28 that the anatase to rutile phase transformation takes place at 600-700 °C, which is higher than the temperature used in this study.

The XRD results of the TiO_2–SiO_2 films in annealing temperature of 500 °C showed a phase distribution of 90:10 (percentage) anatase: rutile, with crystallite size of 25 nm for anatase. The crystallite size of the TiO_2–SiO_2 films at 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 average crystallite size of anatase phase (101) in TiO_2–SiO_2 coating is 22-26 nm.

Characteristic peaks of anatase and rutile were observed in TiO_2-SiO_2 coatings, which are known to contain 90% anatase and 10% rutile. The TiO_2-SiO_2 film on the glass had, however, anatase form. Since anatase TiO_2 was reported to have much higher photocatalytic activity than the rutile phase [29-32], the film was expected to show high photocatalytic activity in this annealing temperature.

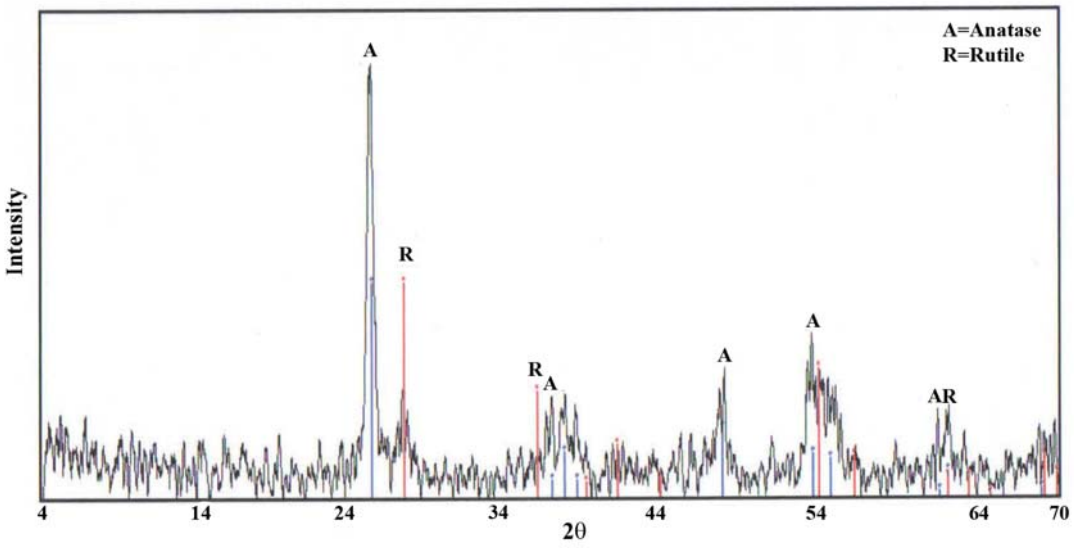

Figure 7: XRD patterns of TiO_2-SiO_2 produced on glass substrates annealed at 500 °C for 30 min at furnace atmosphere.

4. Conclusions

In this study, TiO_2 films were prepared from titanium precursor solution and film structure and morphology was examined. The results can be summarized as follows:

In the present research, SiO_2–TiO_2 transparent thin coatings were successfully prepared on automotive glass using the sol–gel dip-coating technique.

TiO_2-SiO_2 coating attained by sol-gel dip-coating technique was uniform and crack-free. The coatings thickness was desirable and the coating structure and particle size finely suited nanostructure coatings.

XRD shows the crystalline anatase as main phase for TiO_2-SiO_2 films annealed at 500 °C with crystallite size of 22-26 nm according to the Scherrer's equation based on the FWHM for (101) plane of the phase. The phase proportion of anatase and rutile was 90% and

10%, respectively.

The surface morphology results of FE-SEM indicate that the particle size was 22 nm and the particles had uniform distribution.

Acknowledgements

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

5. References

1. B. O. Regan, M. Gratzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films, *Nature,* 353(1991), 737-740.
2. K. Kato, A. Tsuzuki, Y. Torii, H. Taoda, T. Kato, Morphology of thin anatase coatings prepared from alkoxide solutions containing organic polymer, affecting the photocatalytic decomposition of aqueous acetic acid, *J.Mater. Sci.*, 30(1995), 837-841.
3. J. Yu, X. Zhao, J. Du, W. Chen, Preparation, microstructure and photocatalytic activity of the porous TiO_2 anatase coating by sol-gel processing, *J. Sol-Gel Sci. Technol.,* 17(2000), 163-171.
4. N. Barati, M. A. Faghihi Sani, Coating of titania nanoparticles on stainless steel using an alkoxide precursor, *Prog. Color Colorants Coat.,* 2(2009), 71-78.
5. S. M. Hashemi, Kh. Badii, Sh. Abdolreza, Study of immobilization of nano-TiO_2 for environmental aspects on glass by different resin families, *Prog. Color Colorants Coat.,4(2011), 1-6.*
6. K. Nagase, Y. Shimizu, N. Miura. N. Yamazoe, Preparation of vanadium-titanium oxide thin films by sol-gel method and their electro-chromic properties, *J. Ceram. Soc. Jpn.,* 101(1993), 1032-1037.
7. Y. Sorek, R. Reisfeld, I. Finkelstein, S. Ruschin, Sol-gel glass waveguides prepared at low temperature, *Appl. Phys. Lett.,* 63(1993), 3256-3259.
8. H. Tang, K. Prasad, R. Sanjines, F. Levy, TiO_2 anatase thin films as gas sensors, *Sens. Actuators,* 26(1995), 71-75.
9. P. Y. Bourgeois, Y. Kersalé, N. Bazin, M. Chaubet, V. Giordano, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control.,* 50(2003), 1662-1666.
10. D. S. Kommireddy, S. M. Sriram, Y. M. Lvov, D. K. Mills, Stem cell attachment to layer-by-layer assembled TiO_2 nanoparticle thin films, *Biomaterials*, 27(2006), 4296-4303.
11. S. Rasouli, F. Oshani, S. M. Hashemi, Effect of various fuels on structure and photo-catalytic activity of nano-crystalline TiO_2 prepared by micro wave-assisted combustion method, *Prog. Color Colorants Coat.,* 4(2011), 85-94.
12. S. Segota, L. Curkovic, D. Ljubas, V. Svetlicic, I. F. Houra, N. Tomasic, Synthesis, characterization and photocatalytic properties of sol-gel TiO_2 films, *Ceram. Int.*, 37(2011), 1153-1160.
13. J. Chen, C. Poon, Photocatalytic construction and building materials: from fundamentals to applications, *Build. Environ.,* 44(2009), 1899-1906.
14. O. Carp, C. L. Huisman, A. Reller, Photoinduced reactivity of titanium dioxide, *Prog. Solid State Chem.,* 32(2004), 33-177.
15. A. Fujishima, X. Zhang, D. A. Tryk, TiO_2 photocatalysis and related surface phenomena, *Surf. Sci. Rep.,* 63(2008), 515-582.
16. H. Y. Ha, S. W. Nam, T. H. Lim, I. H. Oh, S. A. Hong, Properties of the TiO_2 membranes prepared by CVD of titanium tetraisopropoxide, *J. Membr. Sci.,* 111(1996), 81-92.
17. G. S. Herman, Y. Gao, T. T. Tran, J. Osterwalder, X-ray photoelectron diffraction study of an anatase thin film: TiO_2(001), *Surf. Sci.*, 447(2000), 201-211.
18. K. Kajihara, T. Yao, Macro-porous morphology of the titania films prepared by a sol-gel dip-coating method from the system containing poly(ethylene glycol) III. effect of chemical ad-ditives, *J. Sol-Gel Sci. Technol.,* 16(2000), 257-266.
19. S. Takeda, S. Suzuki, H. Odaka, H. Hosono, Photocatalytic TiO_2 thin film deposited onto glass by DC magnetron sputtering, *Thin Solid Films*, 392(2001), 338-344.
20. D. Bhattacharyya, N. K. Sahoo, S. Thakur, N. C. Das, Spectroscopic ellipsometry of TiO_2 layers prepared by ion-assisted electron-beam evaporation, *Thin Solid Films*, 360(2000), 96-102.
21. Y. L. Wang, K. Y. Zhang, Study of the growth morphology of TiO_2 thin films by AFM and TEM, *Surf. Coat. Technol.,* 140(2001), 155-160

22. C. J. Brinker, G. W. Scherer, sol-gel science: the physics and chemistry of sol-gel processing, Academic Press Inc., San Diego, 1990.
23. S. H. Oh, D. J. Kim, S. H. Hahn, E. J. Kim, Comparison of optical and photocatalytic properties of TiO_2 thin films prepared by electron-beam evaporation and sol-gel dip-coating, *Mater. Lett.,* 57(2003), 4151-4155.
24. S. Vives, C. Meunier, Densification of amorphous sol-gel TiO_2 films: an X-ray reflectometry study, *Thin Solid Films*, 518(2010), 3748-3753.
25. C. J. Brinker, A. J. Hurd, Fundamentals of sol-gel dip-coating, *Journal of Physics III France*, 4(1994), 1231-1242.
26. G. W. Scherer, Sintering of sol-gel films, *J. Sol-Gel Sci. Technol.,* 8(1997), 353-363.
27. K. Endres, M. Mennig, M. Amlung, A. Gier, H. Schmidt, Enhancement of fracture strength of cutted plate glass by the application of SiO_2 sol-gel coatings, *Thin Solid Films,* 351(1999), 132-136.
28. Y. Takahashi, Y. Matsuoka, Dip-coating of TiO_2 films using a sol derived from Ti(O-i-Pr)4-diethanolamine-H2O-i-PrOH system, *J. Mater. Sci.* 23(1988), 2259-2266.
29. R. P. Suri, J. Liu, D. W. Hand, J. C. Crittendon, D. L. Perram, M. E Mullins, Heterogeneous photocatalytic oxidation of hazardous organic contaminants in water, *Water Environ. Res.,* 65(1991), 665-673.
30. R. S. Davidson, C. L. Morrison, J. Abraham, A comparison of the photochemical reactivity of polycrystalline (anatase), amorphous and colloidal forms of titanium dioxide, *J. Photochem.,* 24(1984), 27-35.
31. A. Sclafani, L. Palmisano, M. Schiavello, In-fluence of the preparation methods of titanium dioxide on the photocatalytic degradation of phenol in aqueous dispersion, *J. Phys. Chem.,* 94(1990), 829-832.
32. J. Abrahams, R. S. Davidson. C. L. Morrison, Optimization of the photocatalytic properties of titanium dioxide, *J.* Photochem*., 29(*1985), 353-361.