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SiO_2-TiO_2 Nanostructure Films on Windshields Prepared by Sol-Gel Dip-Coating Technique for Self-Cleaning and Photocatalytic Applications

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Abstract In the present research, automotive windshield samples were successfully coated with SiO_2-TiO_2 nanostructure layer using the sol–gel technique for self- Cleaning and photocatalytic applications. This procedure resulted in transparent, crack-free, self-cleaning, nanostructure SiO_2–TiO_2 films. To prevent the thermal diffusion of the sodium ions from the glass substrate to TiO_2 layer, the SiO_2 layer was pre-coated on the glass by the sol–gel method. The coated samples were dried for 48 hour at room temperature to allow slow solvent evaporation and condensation reactions due to rapid sol–gel reaction of titania precursor. Then, the samples were annealed at 100℃ for 30 min and at the final temperature (500℃ and 700℃) for 30 min immediately. The crystalline structure, surface morphology, photocatalytic activity and hydrophilic properties of the films were investigated using XRD, SEM, FE-SEM, UV–Vis spectrophotometer and contact angle measurement, respectively. The FE-SEM surface morphology results indicate that the particle size increases from 19 to 42 nm by increasing the annealing temperature from 500℃ to 700℃. Likewise, XRD illustrate the crystal anatase and rutile as main phases for SiO_2-TiO_2 films annealed at 500℃ and 700℃, respectively. Increasing heat treatment temperature from 500 to 700℃, decreases the photocatalytic activity and inversely increases of the contact angle of the films.

Keywords SiO_2–TiO_2, Nanostructure Layer, Self-Cleaning Films, Sol–Gel, Dip Coating, Windshield

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 self-cleaning glasses in windshields application, catalysts to reduce pollutants and 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 TiO_2 films as coating for windshields and lateral mirrors to benefit its self-cleaning advantages. Transparent SiO_2-TiO_2 films on glass could form the basis for self-cleaning of indoor windows, lamps or windshields.

Since the past decades, an increasing interest has been devoted to the study of titanium dioxide (TiO_2) thin films. TiO_2 thin films have attracted considerable attention of use such as desensitized solar cells[1], photoelectrodes[1], photocatalysts[2,3], electrochromic 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.

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). 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[9]. The lower amount of the rutile phase of TiO_2, the higher amount of the anatase phase of TiO_2 and the better photocatalytic activity[10-12].

A variety of techniques have been used for the preparation of TiO_2 films including chemical vapour deposition[13,14] sol–gel[2-4,15] sputtering[6,16] and electron-beam evaporation (EBE)[17,18]. TiO_2 film properties strongly depend

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on their microstructure that should be strictly controlled in order to obtain a tailored performance.

Among all the possible techniques existing to elaborate TiO_2 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 TiO_2 films with large specific surface area, which is favourable in achieving good photoactivity[20]. This method allows the modification of the structure and the microstructure of the deposited titanium dioxide playing on the sol composition, the coating parameters and the thermal treatment conditions and etc. Furthermore, the sol–gel process does not necessitate the use of expensive equipments as the case of vacuum deposition techniques[21]. The properties of the sol–gel TiO_2 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 SiO_2-TiO_2 films for advanced windshields to benefit the self-cleaning applications. Specifically, annealing temperature as the key feature of the layer which affects performance, microstructure and the fundamental phase that must be considered, is addressed.

2. Experimental

2.1. Materials

Titanium tetra isopropoxide[1] (TTIP, 99 %, PANREAC) and Tetraethyl ortosilicate[2] (TEOS, 98%, ACROS) were used as precursors. 2-propanol[3] (99.7%, MERCK) and ethanol[4] (96%, MRECK) served as solvents; hydrochloric acid (HCL, 37%, MERCK) was used as a catalyst. diethanolamine[5] (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 procedures for the silica sol preparation and its characteristics were presented in detail elsewhere[24]. 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 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.

[1] -($C_{12}H_{28}O_4Ti$) or $Ti(OC_3H_7{}^i)_4$
[2] -($C_8H_{20}O_4Si$) or $Si(C_2H_5O)_4$
[3] - $CH_3CH(OH)CH_3$
[4] - C_2H_5OH
[5] - $C_4H_{11}NO_2$

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 SiO_2-TiO_2 films. At first, substrates were cleaned in an ultrasonic cleaner with de-ionized water and then with acetone. Subsequently the prepared specimens were heated at the temperature of 60℃ for 1h and immediately coated.

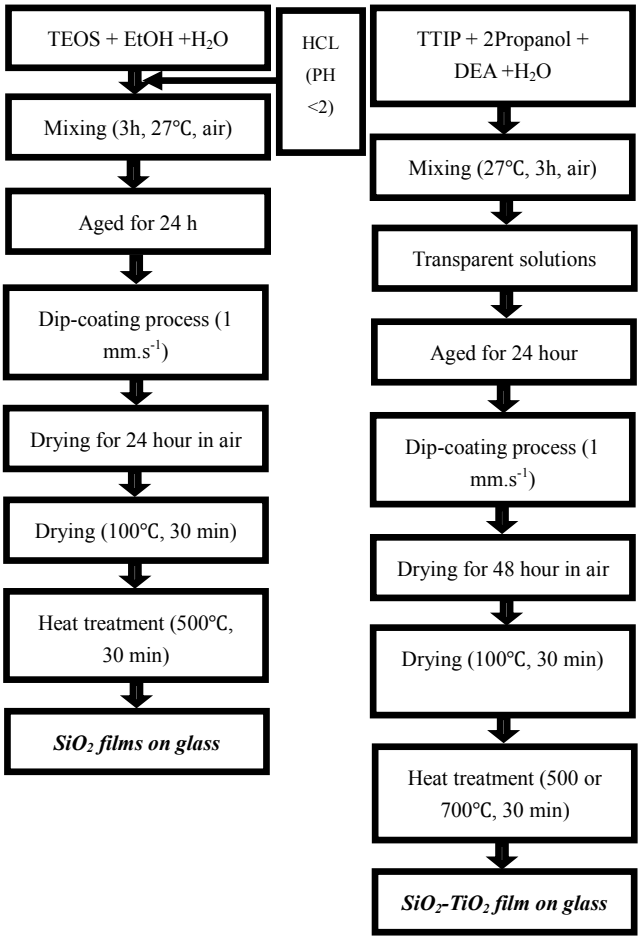

Figure 1. Procedure used in this paper (left: preparation process of SiO_2 films, right: the preparation process of SiO_2-TiO_2films)

2.4. Dip Coating

The substrates were dipped in the sol and withdrawn at a speed of 1 $mm.s^{-1}$ to make a gel film. The coated films were dried for 48 hour at room temperature 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℃. min^{-1} until 100℃; hold at this temperature for 30 min. The coated substrates were dried at 100℃ 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℃. min^{-1} to the final temperature (500 and 700℃) and hold at this temperature for 30 min to accomplish the crystallization of gel films. Finally, the films were cooled in the furnace to room temperature. A flow chart of this method is presented in Figure. 1.

2.5. Characterization of TiO_2 Films

The main phase present was identified and the crystal size of the SiO_2-TiO_2 films was determined by X-ray diffractometer (XRD) (D8 Advance, Bruker Co., Germany) using monochromatic Cu–Kα radiation operated at 40 kV and 30 mA at the scan speed of 0.02 sec per step with an increment of 0.02° per step. The crystal size of the SiO_2 - TiO_2 films is calculated using the Scherrer's equation based on the full peak width at half maximum intensity (FWHM).

Film morphology was characterized by Scanning Electron Microscopy (SEM; Tescan model Vega-II) and Field-Emission-Scanning Electrons Microscopy (FE-SEM, S-4160). Photocatalytic activity of the SiO_2-TiO_2 films was evaluated by investigating degradation of methylene blue (MB), which was used to represent a pollutant. For the photo degradation investigation, the SiO_2-TiO_2 films on glass substrates were immersed in an aqueous solution of MB (6.25×10-5 M) then irradiated with UV light for 2 h. After the radiation, degradation of the MB was determined by measuring absorbance of the MB of each decanted solution using UV–vis spectrophotometer (SERIES C-2040) at maximum wavelength of λ_{max} = 664 nm. The contact angle for water was determined using an OCA 15- plus (Data-physics).

3. Results and Discussion

3.1. Surface morphologies of SiO_2–TiO_2 films

The surface morphology of the SiO_2-TiO_2 films were examined using SEM. Figure. 2 shows SEM micrographs of the SiO_2-TiO_2 films on substrate annealed at (A) 500℃ and (B) 700℃ 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 Figure. 2). This is due to substrate plasticity and softening at the temperature of 700℃.

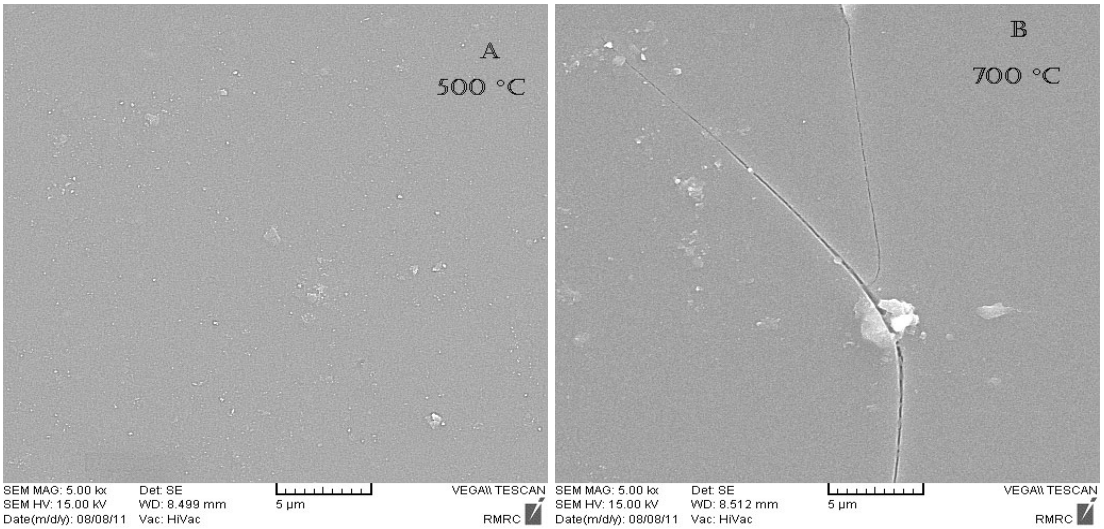

Figure 2. SEM micrographs of SiO_2-TiO_2 films annealed at (A) 500℃ (B) 700℃

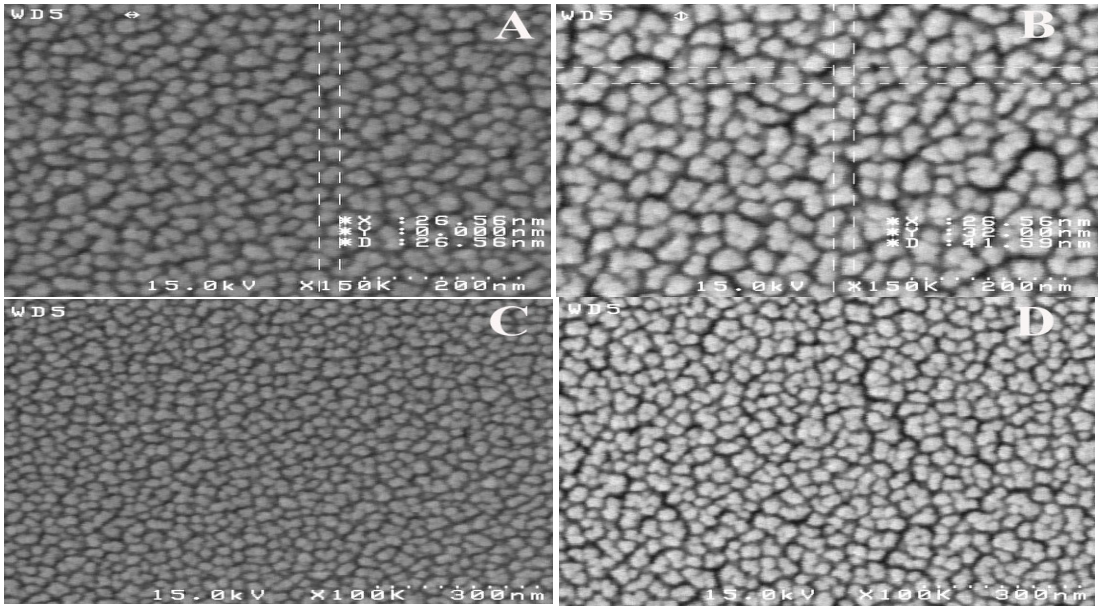

Figure 3. FE-SEM micrograph of a SiO_2-TiO_2films annealed at (A,C) 500℃, (B,D) 700℃

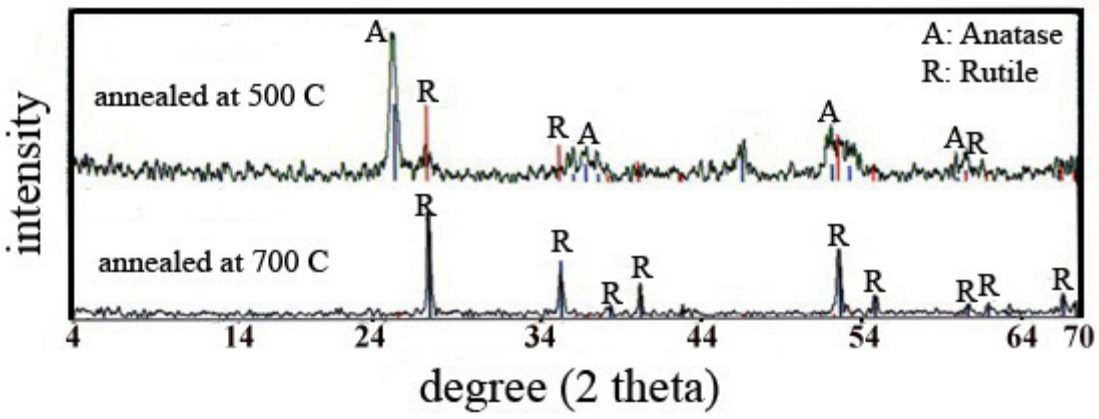

Figure 4. XRD patterns of SiO_2-TiO_2 films produced on glass Substrates annealed at 500°C and 700°C for 30 min in air

Figure. 3 shows FE-SEM images of SiO_2-TiO_2 films prepared at 500°C and 700°C at two different magnifications of 100,000 and 150,000. The FE-SEM images revealed that the surface morphology of the SiO_2-TiO_2 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 (Figure. 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 (Figure. 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. These FE-SEM images revealed that the surface morphology of the SiO_2-TiO_2 films annealed at 500°C and 700°C has appropriate distribution of TiO_2 particles without any agglomeration effects which can weaken coating properties.

3.2. Crystal Structure of SiO_2-TiO_2 Films

In order to compare the crystalline composition and crystal size of the films prepared at different annealing temperatures (500 and 700°C), XRD test was employed. Figure. 4 represents results of XRD analysis for the SiO_2-TiO_2 films.

The XRD pattern clearly shows that the main peak of films annealed at 500°C is at 25.28, which corresponds to anatase (101) plane. The main peak of Films annealed at 700°C is at 27.44, which corresponds to rutile (110) plane. The peak corresponding to rutile phase 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 in this research) cannot lead to anatase-to-rutile crystal phase transformation. On the other hand, high annealing temperatures (for instance, 700°C in this study) have led to the transformation of anatase to rutile. One can deduce from[25] that the anatase to rutile phase transformation take place at temperatures between 600-700°C. There is a decrease in amount of anatase phase in the crystalline plane of (101) after increasing annealing temperature from 500 to 700°C.

The XRD results of the SiO_2-TiO_2 films at annealing temperature of 500°C showed a phase distribution of 91:9 of anatase:rutile phases, with crystal size of 21 and 9 nm, for anatase and rutile, respectively. Also XRD results of the SiO_2-TiO_2 films at annealing temperature of 700°C showed a phase distribution of 6:94 of the phase anatase:rutile, with crystal size of 52 nm for rutile. Results on average crystal size of the SiO_2-TiO_2 films at annealing temperature 700°C of rutile phase (110) derived from XRD patterns revealed rutile as the main crystal phase, with a fundamental crystal size of 52 nm.

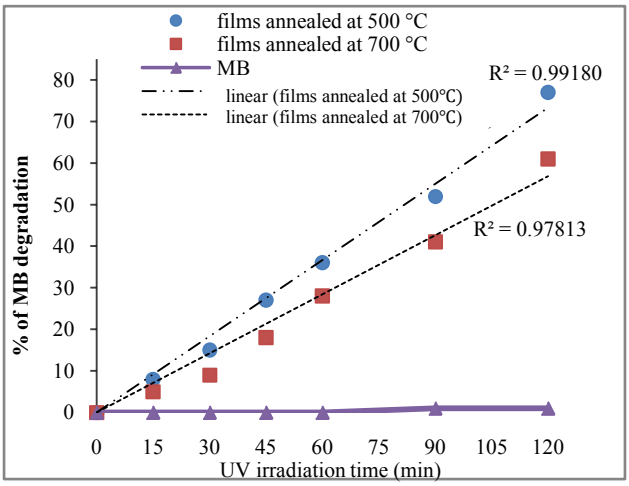

Figure 5. A comparison of photocatalytic activities of the SiO_2-TiO_2 films annealed at (a) 500°C (b) 700°C

3.3. Photocatalytic Activities of SiO_2-TiO_2 Films

Figure. 5 shows the dependence of the MB concentration in the solution for the SiO_2-TiO_2 films annealed at 500°C and 700°C on the UV irradiation time. For both films, the concentration of MB in the solution decreases. As shown in Figure. 5, there was no direct photolysis of MB in the absence of the SiO_2-TiO_2 films. The SiO_2-TiO_2 films annealed at 500°C exhibits higher degradation rate. This phenomenon seems to be due to the higher amount of the anatase phase of TiO_2 and lower amount of rutile phase of TiO_2. High hydrophilicity of coatings annealed at 500°C compared to those annealed at 700°C support this reason. The photocatalytic

activity of the SiO_2-TiO_2 films annealed at 700℃ is lower being comparable with the SiO_2-TiO_2 films annealed at 500℃. The differences in photocatalytic activity could be contributed to the differences in phases which mainly exist in each films. The photocatalytic activity of the SiO_2-TiO_2 films shows a close dependence on heat treatment temperature.

The photocatalytic degradation of the MB dye follows the Langmuir–Hinshelwood kinetics model given by the equation (1)[9]:

$$-Ln\left(\frac{C_0}{C}\right) \cong Kt \quad (1)$$

Where C_0 is the MB initial concentration, C is the MB concentration (mgL^{-1}) at a time t (min) and K is the rate constant in min^{-1}.The rate constant K from (1) is evaluated through the linear regression of $Ln(C/C_0)$ versus time. According to the R^2 values of 0.99180 and 0.97813 for films respectively annealed at 500℃ and 700℃, the linear relationship of Ln(C/C0) with time is proved (see Figure. 5). The results show that the photocatalytic degradation of the MB can be described by the Langmuir–Hinshelwood kinetics model[9].

3.4. Surface Wettability of SiO_2-TiO_2 Films

Surface wettability is a crucial factor for the self-cleaning of SiO_2-TiO_2 films when applied on windshields. A super hydrophilic surface favors the spread of water and the contaminant on the surface can be removed easily by the rainwater[26].

Figure. 6 shows the contact angle of 4 µL water on the SiO_2-TiO_2 films. The contact angles less than 10° are recorded as zero, as the OCA 15- plus was not able to accurately measure contact angles below 10°.

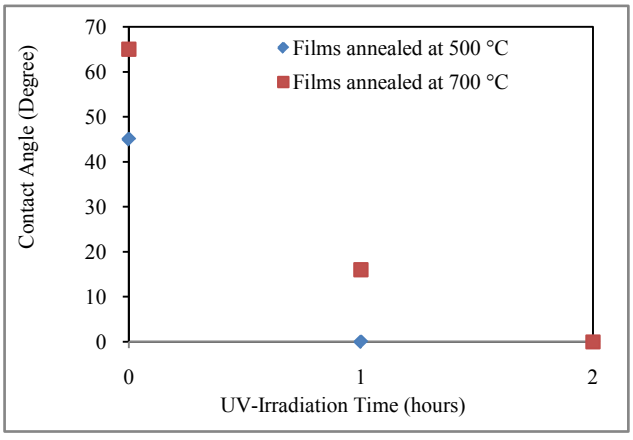

Figure 6. Changes in the water contact angle of the SiO_2-TiO_2 films annealed at 500℃ and 700℃ (in a dark and after 1, 2 hours UV irradiation)

In dark (without UV irradiation), the water contact angle on the SiO_2-TiO_2 films annealed at 500℃ and 700℃ is 45° and 65°, respectively. Without UV irradiation, the surface wettabilities of the SiO_2-TiO_2 films annealed at 500℃ and 700℃ are different. An increase in the heat treatment temperature has led to an increase in the contact angle. After 1h UV irradiation, the water contact angle on SiO_2-TiO_2 film annealed at 500℃ and 700℃ both decrease to 0° and 16° respectively. After 2 h UV irradiation, both films showed super hydrophilic with contact angles less than 10°. Such an excellent surface wettability is very favorable for the self-cleaning function when the SiO_2-TiO_2 films are applied windshields.

5. Conclusions

In the present research, SiO_2–TiO_2 nanostructure films were successfully coated on windshields using the sol–gel technique for self-cleaning applications. This paper presents the annealing temperature effect on the properties of the SiO_2-TiO_2 films. This research proved that annealing temperature is an important parameter which affect the structure; surface morphology, photocatalytic activity and surface wettability of the SiO_2-TiO_2 films.

The FE-SEM surface morphology results indicate that the particle size increases from 19 to 42 nm by increasing the annealing temperature from 500℃ to 700℃. The SEM surface morphology results of the SiO_2-TiO_2 films annealed at 500℃ was uniformly and crack-free.

XRD shows the crystal anatase and rutile as main phases for SiO_2-TiO_2 films annealed at 500℃ and 700℃, respectively. Films annealed at temperatures below 100℃ are not adhesive, do not adhere well to the glass substrate, and flake off into the solution. Annealing at 200℃ produces a film that can be removed from the surface by soft scratching. Films annealed at 500℃ are adherent. Annealing at 700℃ is not suitable and practical, because at this temperature glass substrate begins to soften and lucidity reduced. 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 SiO_2-TiO_2 films.

Increasing heat treatment temperature from 500℃ to 700℃ decreases the photocatalytic activity of the films. A clear diminution in the photocatalytic activity occurred at the temperature of 700℃. This can be assumed to result from the increasing conversion from anatase into rutile.

In dark (without UV irradiation), the SiO_2-TiO_2 films annealed at 500℃ with anatase phase are almost hydrophilic with the contact angle 45°, those annealed at 700℃ with rutile phase are relatively hydrophobic with the contact angle 65°. This change in contact angle is clearly due to an increase in the heat treatment temperature. After 1h UV irradiation, the wettabilities of the SiO_2-TiO_2 films become almost same. After 2 h UV irradiation, both films show super hydrophilic with contact angles less than 10°.

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REFERENCES

[1] O'Regan, B and Gratzel, M., 1991, A low-cost, high- efficiency solar cell based on dye-sensitized colloidal TiO_2 films, Nature, 353, 737.

[2] Kato, K., Tsuzuki, A., Torii, Y. and Taoda, H., 1995, Morphology of thin anatase coatings prepared from alkoxide solutions containing organic polymer, affecting the photocatalytic decomposition of aqueous acetic acid, Journal of Materials Science, 30(3), 837-841.

[3] Jiaguo Yu, Xiujian Zhao, Jincheng Du and Wenmei Chen, 2000, Preparation, Microstructure and Photocatalytic Activity of the Porous TiO_2 Anatase Coating by Sol-Gel Processing, Journal of Sol–Gel Science Technology, 17 (2), 163-171,

[4] Nagase, K., Shimizu, Y., Miura, N. and Yamazoe, N., 1993, Preparation of Vanadium-Titanium Oxide Thin Films by Sol-Gel Method and Their Electrochromic Properties, Journal of Ceramics Society, Japan, 101.

[5] Sorek, Y., Reisfeld, R., Finkelstein, I. and Ruschin, S,. 1993, Sol-gel glass waveguides prepared at low temperature, Applied Physics Letters, 63, 3256.

[6] Tang, H., Prasad, K., Sanjinés, R. and Lévy, F., 1995, TiO_2 anatase thin films as gas sensors, Sensors and Actuators B: Chemical, 26(1–3), 71-75.

[7] Kersale, Y., 2003, Cryogenic monolithic sapphire-rutile temperature compensated resonator oscillator, IEEE Trans. Ultrason. Ferroelectr. Freq. Control., 50, 1662.

[8] Kommireddy, Dinesh S., Sriram, Shashikanth M., Lvov, Yuri M. and Mills, David K., 2006, Stem cell attachment to layer-by-layer assembled TiO_2 nanoparticle thin films, Biomaterials, 27(24), 4296-4303.

[9] Šegota, S., Ćurković, L., Ljubas, D., Svetličić, V., Houra, I.F. and Tomašic, N., 2011, Synthesis, characterization and photocatalytic properties of sol–gel TiO2 films, Ceramics International, 37(4), 1153–1160.

[10] Fengna Chen, Xudong Yang and Qiong Wu, 2009, Antifungal capability of TiO_2 coated film on moist wood, Building and Environment, 44(5), 1088-1093.

[11] Carp, O., Huisman, C.L., Reller, A., 2004, Photoinduced reactivity of titanium dioxide, Progress in Solid State Chemistry, 32(1–2), 33-177.

[12] Fujishima, A., Zhang, X. and Tryk Donald A., 2008, TiO_2 photocatalysis and related surface phenomena, Surface Science Reports, 63(12), 515-582.

[13] Heung Yong Ha, Suk Woo Nam, Tae Hoon Lim, In-Hwan Oh and Seong-Ahn Hong, 1996, Properties of the TiO_2 membranes prepared by CVD of titanium tetraisopropoxide, Journal of Membrane Science, 111(1), 81-92.

[14] Herman, G.S., Gao, Y., Tran, T.T., Osterwalder, J., 2002, X-ray photoelectron diffraction study of an anatase thin film: TiO_2 (001), Surface Science, 447, 201-211.

[15] Kajihara, K. and Yao, T., 1999, 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, 16(3), 257-266.

[16] Takeda, S., Suzuki, S., Odaka, H. and Hosono, H., 2001, Photocatalytic TiO_2 thin film deposited onto glass by DC magnetron sputtering, Thin Solid Films, 392(2), 338-344.

[17] Bhattacharyya, D., Sahoo, N.K., Thakur, S. and Das, N.C., 2000, Spectroscopic ellipsometry of TiO_2 layers prepared by ion-assisted electron-beam evaporation, Thin Solid Films, 360(1–2), 96-102.

[18] Leprince-Wang, Y. and Yu-Zhang, K., 2001, Study of the growth morphology of TiO_2 thin films by AFM and TEM, Surface and Coatings Technology, 140(2), 155-160.

[19] C.J. Brinker and G.W. Scherer, Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing, San Diego, USA, Academic Press Inc., 1990.

[20] Oh, S.H., Kim, D.J, Hahn, S.H. and Kim, E.J., 2003, Comparison of optical and photocatalytic properties of TiO_2 thin films prepared by electron-beam evaporation and sol–gel dip-coating, Materials Letters, 57(26–27), 4151-4155.

[21] Vives, S. and Meunier, C., 2010, Densification of amorphous sol–gel TiO_2 films: An X-ray reflectometry study, Thin Solid Films, 518(14), 3748-3753.

[22] Brinker, J. and Hurd, C.J., 1994, Fundamentals of sol-gel dip-coating, J. Phys. III France, 4, 1231.

[23] Scherer, G.W., 1997, Sintering of Sol-Gel Films, Journal of Sol-Gel Science and Technology,8(1-3), 353-363.

[24] Endres, K., Mennig, M., Amlung, M., Gier, A. and Schmidt, H., 1999, Enhancement of fracture strength of cut plate glass by the application of SiO_2 sol-gel coatings, Thin Solid Films, 351(1–2), 132-136.

[25] Takahashi Y. and Matsuoka, Y., 1988, Dip-coating of TiO_2 films using a sol derived from Ti(O-i-Pr)4-diethanolamine-H_2O-i-PrOH system, Journal of Materials Science, 23(6), 2259-2266.

[26] Liu, Z., Zhang, X., Murakami, T. and Fujishima, A., 2008, Sol– gel SiO_2/TiO_2 bi-layer films with self-cleaning and anti-reflection properties, Solar Energy Materials & Solar Cells, 92, 1434– 1438.