INVESTIGATION OF PHOTOCATALITIC PROPERTIES OF TIO_2 THIN FILM COATED ON PLEXY GLASS

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Abstract

In this study, glass surface is coated with thin films of TiO2 by using sol-gel route. TiO2 chemicals were used as precursors at the solutions prepared for film coating, and also methanol and acetyl acetone were used as solvent and chelating agent respectively. After the glass samples were dipped in to prepared solutions by using a special apparatus, they were taken into the preheated (500 °C) vertical furnace to dry, and then they were annealed at the same temperature. The thin films formed on the glass surface were characterized through the instrument of X-ray photoelectron spectrometer (XPS), thermogravimetric and differential thermal analysis (TG-DTA), Ellipsometer and Spectrometer test devices. Wet angles of thin films coated with different dipping number and annealed at different temperature, were measured by dropping 1 microliter distilled water (UP_ ultra-pure). The water contact angle between the droplet and the surface of the sample was measured. Wet angle did not change with the number of dipping number. However, the angle of contact change with the temperature of crystallization. Finally, the TiO2 thin film coated glass samples were subjected to soot with the flame of a candle with a special apparatus. After sooting, TiO2-coated glass samples were subjected to UV light for 24-48-72-96-120 hours. UV exposure samples were pictured with same conditions in every 24 hours. Cleaning affect of the surface were identified in a visible way.

Keywords: Self cleaning, sol-gel method, glass surface coating, lotus effect

1. INTRODUCTION

There has been a great interest for self-cleaning surfaces for the last decade [1]. Self-cleaning thin film surfaces have been commercially used for optically transparent surfaces such as optical lenses, window glasses for cars and houses, architectural decoration products, shower cabins, solar panels, traffic signal lambs, mirrors in hospitals and green house glasses as well as textile products. Since 1969, it has been known that TiO_2 separates water into oxygen and hydrogen by illumination [1]. After this point, research about photocatalitic activity of TiO_2 has been increasingly continued. TiO_2 has three types of crystal structures: anatase, rutile and brookite [2]. Up to date, there has been an extensive researches performed on anatase and rutile structures [1].

Coated film with nano sized thicknesses on glass does not destroy the transparency of glass while it gives self cleaning property. When TiO_2 is exposed to the UV light, it produces free radicals by reacting with oxygen and water in the air. In addition to that, a photocatalytic reaction is occurred on its surface. Electrons move to conduction band from valance band to create electron (e^-) - hole (h^+) pairs. Electrons and holes that are diffused on to the surface of semiconductor interact with water and oxygen molecules are hanged on by emitting of light. During this interaction, electrons and holes act as acceptors and donors respectively. Holes provide hydroxyl (OH-) radicals by reacting with H_2O. Electrons provide superoxide ($O2^{-}$ •) radicals by reacting with O_2. Hydrogen ions (H^+) that occur within the reaction of holes and H_2O produces hydrogen peroxide by reacting with electrons. Photocatalytic processes of TiO_2 include chemical steps that produce reactive products such as hydrogen radicals, hydrogen peroxide and superoxide. These reactive oxides damage the organic molecules and micro organisms [3-4].

Coating methods of TiO_2 can be classified into two groups such as wet and dry coating methods [5]. Chemical vapor deposition, physical vapor deposition and direct deposition methods can be mentioned as dry while sol-gel method can be remembered as wet [6].

2. EXPERIMENTAL METHOD

In this study, 18 x 18 x 0.5 mm sized silica glasses are coated. Four different Ti precursors are tried to prepare a coating solution. Titanium nitride is used first but it is not possible to dissolve it in solvent and chelating agent. Secondly, Titanium acetate is tried and a transparent solution is obtained. However a homogenous coating cannot be achieved. Titanium metoxide is successfully used as a precursor for sol-gel coating. In another work, It is also used as a precursor for the same purpose [7]. XPS and TG/DTA analyses are carried out on the samples that are coated with this solution. Titanium di-isopropoxyde is also used as a precursor and a transparent solution is obtained by completely dissolving it in solvent and chelating agent mixture. However, a homogenous coating is not achieved by using this solution too. Finally Titanium butoxide is used and a successful coating is carried out by using this solution. This precursor is also used successfully in another work [8]. The thin films that are prepared with Titanium butoxide is used for characterizing by means of wetting angle, thickness measurement, optical transparency and UV exposure. The flowchart of the coating and characterizing process is given in Figure 1.

3. RESULTS AND DISCUSSION

3.1. XPS Scanning

Elemental bonding analyses of the coated film are carried out by using Termo - Xray photoelectron spectrometry device with Al K_α monochromatic radiation (1486.69 eV).

XPS scanning of the titanium dioxide thin film is given in Figures 2a, 2b and 2c. In these figures, the characteristic limits of titanium, growth parameters of oxygen and carbon can be seen easily. By using Ti2p, O1s and C1s peak variations, chemical ratios of the surface compositions can be detailed. Although there is no carbon in thin film, XPS scan gives some peaks belong to the carbon. It is probably due to the contamination of the surface. Similar carbon existence is indicated by a peak in another study, even though carbon is not included as one of the starting materials [9].

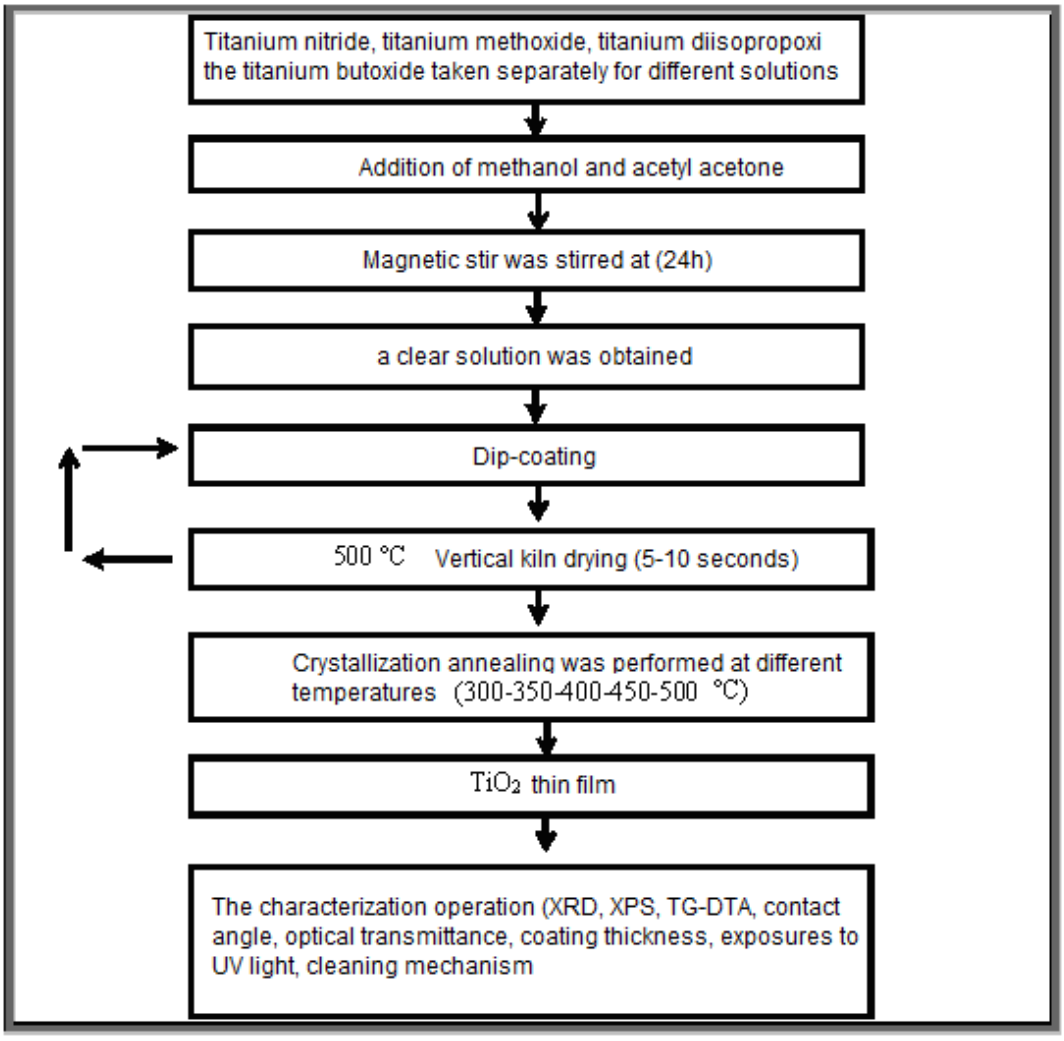


Fig. 1. Solution preparation and film characterization process flowchart

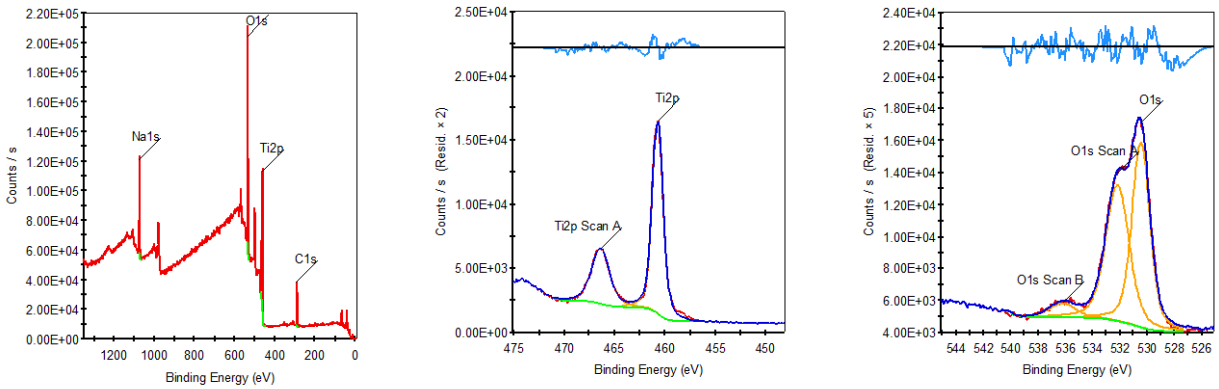


Fig. 2 XPS scanning graph of coated film.
a) 3 times dipped then annealed at 400 °C for crystallization
b) Ti2P and c) O1s scanning graphs of 3 times dipped and annealed at 500°C thin film.

XPS scan shows that plexy glass is coated with thin film TiO_2. In figure 2a, for the peak of Ti2p3/2, bonding energy is found as 459,2 (eV) and the full width of the peak is 1,5° ±0,1. For the peak of Ti2p1/2, bonding

energy is found as 464,7 ±0,1 (eV). Distance between Ti2p3/2 and Ti2p3/2 peaks is 5,7 (eV). O1s bonding energy is 530,5 ± 0,1 (eV). Figure 2c shows the oxygen content of the scanned surface. O1s (Ti-O) at 529,7 eV is the characteristic TiO_2 peak and that peak is the evidence for the existence of TiO_2 phase. The joined peak at 532,0 eV of O1s may be attributed to different oxidized hydrocarbons (contamination).

The composition and chemistry of the glass surface coated thin films of TiO_2 is investigated by XPS. The photoelectron peak for Ti2p originates from the Ti-O bond in the form of TiO_2 (IV) and Ti_2O_3 (III). Ti2p core level involves two main peaks which are $Ti2P_{3/2}$ and $Ti2P_{1/2}$. $Ti2P_{1/2}$ peak is located at 460 eV.

The distance between Ti2p3/2 and Ti2p3/2 peaks is 5.7 (eV). O1 binding energy is 530.5 ± 0,1 (ev) [9]. Figure 2c shows the oxygen content of the coating material. O1s (Ti-O) component of the resulting peak value of 530 eV is the peak of TiO_2 and this peak indicates the presence of TiO_2 phase. O1s (-OH) which is the second component of 532 eV peak shows the percentage of oxygen on the surface of –OH and this result shows the improvement in the photocatalytic process. The highest point of this value (O1s) corresponds to 533.0 eV [10]. XPS measurements show that the plexy glass is homogeneously coated with TiO_2 thin film.

3.2. Thermogravimetry and Differential Thermal Analysis (TG-DTA)

Coating material is also analyzed by means of TG and DTA. Solution is dried at 60 °C for 24 hours to powder then TG and DTA are applied between 50 °C - 800 °C with a heating rate of 10 °C/min. Thermal tests are carried out under Argon atmosphere with a flow rate of 130 ml/min.

Figure 3 shows the TG-DTA graph of TiO_2 powder received by drying TiO_2 coating solution. As it is seen from the graph, analysis gives 3 exothermic and 1 endothermic reaction peaks. The graph starts with an endothermic reaction coming from the water evaporation in the beginning. The first exothermic reaction occurs at temperature between 250–280 °C. Weight loss increases during these temperatures and transformation from amorphous to crystalline structure starts. Amorphous TiO_2 transforms into brookite structure. Second exothermic reaction occurs at temperature between 290 – 310 °C. At temperature interval of 440 – 460 °C, third exothermic reaction takes place. The last exothermic reaction is relatively a small one. The last two reactions are indicating the transformations of brookite structure into first anatase and then rutile structure respectively.

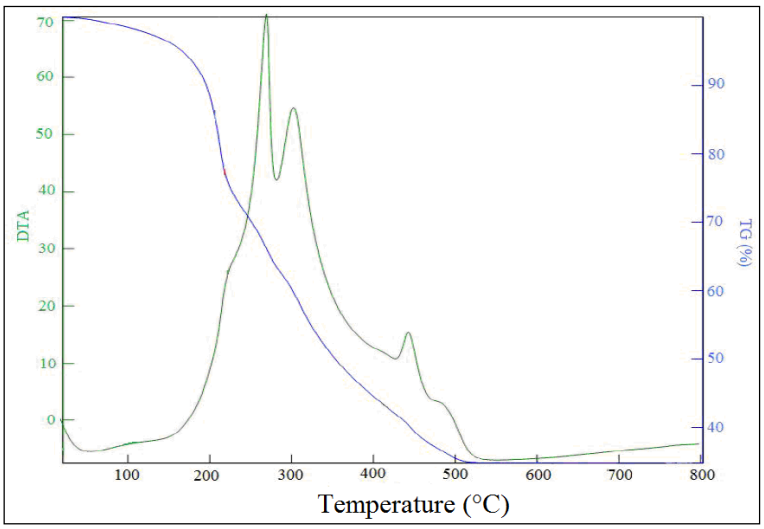


Fig. 3 TG/DTA graph of TiO_2 powder received by drying TiO_2 solution

During the endothermic reaction, %5 of weight loss occurs due to residual humidity inside the dried TiO_2 powder. %32 weight loss is also occurred during the first exothermic reaction at temperature between 250 – 280 °C. Total weight loss is about %65 during TG analysis. TG analysis indicates that dried powder has still

both some amount of residual humidity and non TiO_2 content. Peaks in DTA analysis are the evidence of transformation from amorphous to crystalline structure [11].

3.3 Thickness measurement

Thickness of the coated films is measured by using a V-VASE HS190 Woollam Ellipsometer. Five samples with five different thicknesses are measured. Samples are heat treated at 400 °C for 30 minutes for crystallization after coated by 1 to 5 times dipping.

As it can be observed from Figure 4, the increase in thickness is proportional to the dipping number. Thickness achieved per dip is nearly the same for the first three dips while 4th and 5th dipping increments are different. Such variation could be expected in sol-gel dip-coating method because of the non-balanced coating conditions [7].

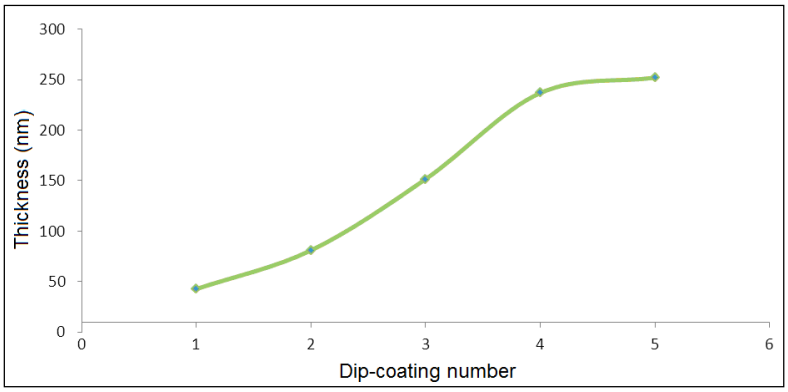


Fig. 4. Film thickness variation with dipping numbers

As it is seen on Landau-Levich equation (eq. 1), the film thickness is directly proportional to viscosity, drawing speed and inversely proportional to liquid-gas interface, gravity and liquid density. These factors are effective on the film thickness:

$$h = 0.94 \frac{(\eta V)^{\frac{2}{3}}}{(\gamma_{LV}^{\frac{1}{6}} (\rho g)^{\frac{1}{2}}} \qquad \text{(eq.1)}$$

where h is the coating thickness, η is viscosity, V is drawing speed, γ_{LV} is the liquid-vapour surface tension, g is gravity and ρ is density.

3.4 Optical transparency

Transparency and reflection characteristics of coated film are measured using a Varian Cary 5000 Spectrophotometer. Two groups of coated samples are studied: first group is not annealed and second group is annealed for crystallization. Each group has 8 samples that are coated with one to eight dipping.

It can be seen from the figure that, 1 time-dipped coat is transparent for the wavelengths bigger than 350 nm meanwhile one single dip coat (approximately 60 nm thickness) leads a transparency lose of 20%. This lose can be increased by increasing the film thickness (Figures 5 and 6).

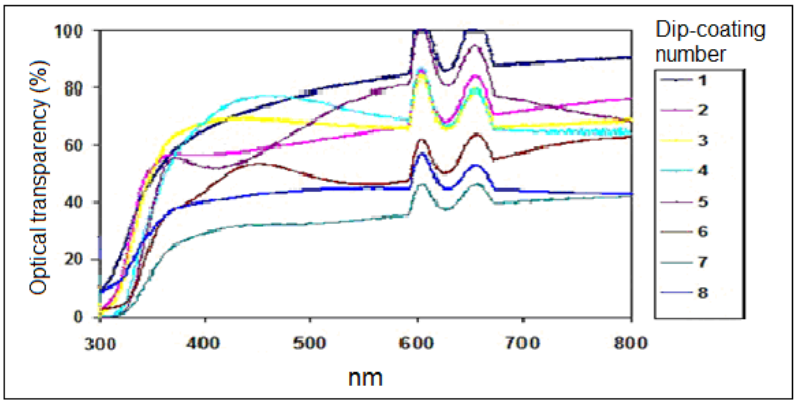


Fig. 5. Optical transparency results of TiO_2 films on glass. Films were annealed at 500 °C for two hours

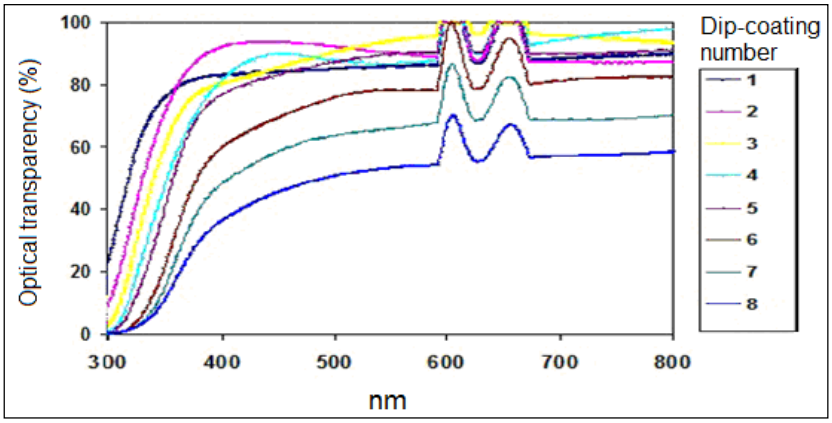


Fig. 6. Optical transparency results of TiO_2 films on glass. Films were not annealed

After 8 dips, 400 nm thicknesses can be assumed approximately and 30% of the transparency still exists. While the transparency lost is very high and linear in the beginning (1-5 dips), proportion of the transparency lost decreases for later dips (6-8 dips). Transparency lost is changing with dip number in a similar way for both annealed and non-annealed coatings. Similar work has been done before and they get the similar result for transparency lost [12].

As can be seen from the results, optical transparency lost is nearly 80% for 8 dip of non-annealed coatings. In annealed coatings, transparency lose increases to 70% after 8 dips. This shows that the annealing of TiO_2 coated glass decreases the optical transparency. These decrements can be attributed to the increased vacancies caused by crystallization annealing [8].

3.5 Wetting angle

Wetting angles of samples are measured with a contact angle measurement system (OCA30) in National Nanotechnology Research Center (UNAM). The coating procedure is carried out for different number of coatings and crystallization temperatures. The measurement is repeated three times for each glass sample surface. Tables 1 and 2 list the results of the average wetting angles.

Wetting angle data cannot be obtained at 300 °C due to the strong affinity of thin film surface to water. Superhydrophilic surface allows water to spread completely across the surface and it has a water contact angle of 0°. Samples coated with TiO_2 thin film by two dips and annealed at 300 °C show superhydrophilic behaviour.

The droplet spreads by wetting a large area of the surface, causes the wetting angle less than 90 degrees which the surface is considered hydrophilic or water-loving. As it is seen in Figure 7 a and b, two times coated TiO_2 thin film shows good hydrophilic property with low wetting angle after heat treated at 500 °C. Decrease

in water contact angle on TiO_2 coated thin film is observed and this result is in agreement with data obtained by Karakas et al. [13].

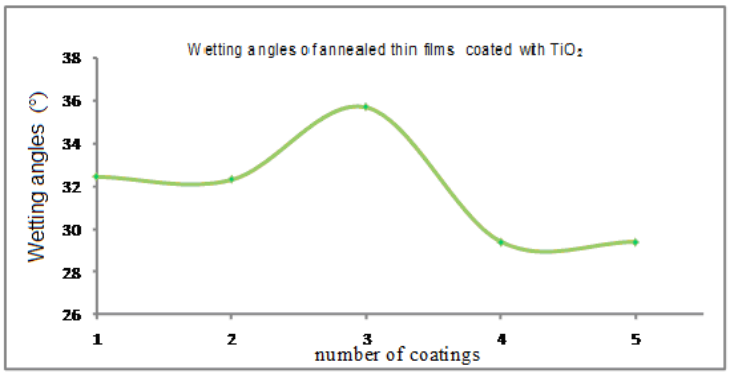


Fig. 7.a) Wetting angles of annealed thin films two times dip-coated with TiO_2 at 300 °C

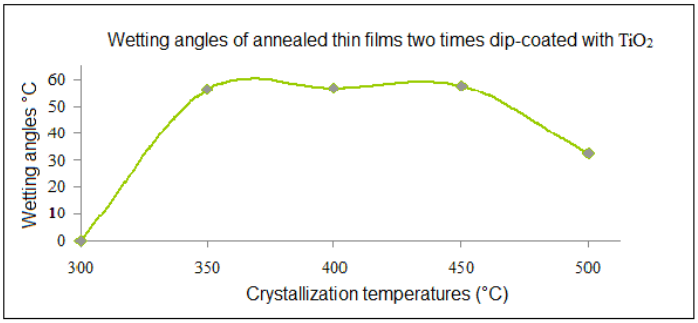


Fig. 7.b) Wetting angles of annealed thin films two times dip-coated with TiO_2 at 500 °C

3.6 Exposing the Sample to Ultraviolet light

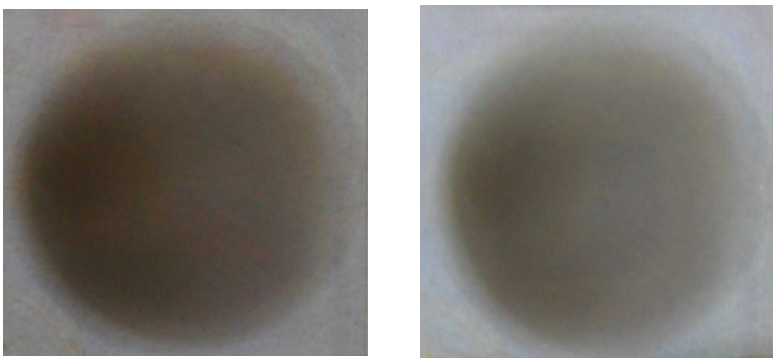
Thin films to be subjected to this test are obtained with two times dip coating at 300°C and four times dip-coating at 500°C by sol-gel method. TiO_2 thin film coated glass samples are exposed to soot dirty in the light of the candle with a special apparatus. The surface of the TiO_2 thin film glass samples subjected to soot dirty are exposed to UV light (8 W) for 24-48-72-96-120 hours. The self cleaning effect and changes in properties of these samples are examined. Two times dip coated thin films which are exposed to soot dirty show obvious self-cleaning effect under UV light for 120 hours (Figures 8 and 9).

Uncoated glasses are soothed and exposed to UV light (Figure 10) to show the distinction from coated glasses. After 120 hours of exposure, there is no indication of cleaning throughout the surface. The comparison of TiO_2 coated thin film and uncoated glass samples after exposure to soot dirty results in the surface of TiO_2 coated thin film has a clear self-cleaning effect property.

a) 0 hour	b) 24 hours	c) 48 hours

a) 72 hours	b) 96 hours	c) 120 hours

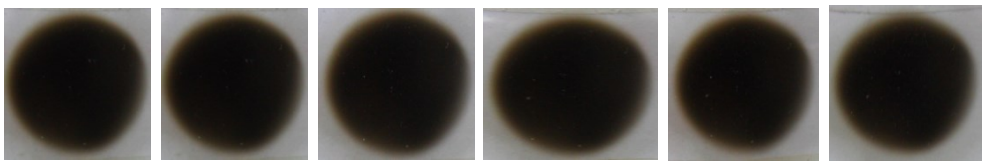
Fig. 8 TiO_2 thin film on glass is obtained with four times dip-coating at 500°C by sol-gel method. The surface of the TiO_2 thin film glass samples subjected to soot dirty were exposed to under UV light (8 W) for of 0- 24-48-72-96-120 hours comparison



a) 0 hour	b) 120 hours

Fig. 9 TiO_2 thin film on glass is obtained with four times dip-coating at 500°C by sol-gel method. The surface of the TiO_2 thin film glass samples subjected to soot dirty were exposed to UV light (8 W) for 120 hours comparison. It is compared with non exposed one.

The UV excites electron and hole pairs and these photogenerated electrons react with molecular oxygen to produce radical anions ($.O_2^-$). The photogenerated holes react with water to produce hydroxyl radicals (OH). These two reactive radicals decompose organic compounds. The photocatalytic activity of TiO_2 depends on crystal structure (anatase or rutile), surface area, size distribution, pore structure and density of hydroxide group [14]. These factors cause to form electron hole pairs affecting organic material. Finally, the contamination on the surface of TiO_2 coated thin films is decomposed and disappears.



a) 0 hours b) 24 hours c) 48 hours d) 72 hours e) 96 hours f) 120 hours

Fig. 10 The surface of the uncoated glasses thin film glass samples subjected to soot dirty were exposed to under UV light (8 W) for of 24-48-72-96-120 hours.

Electrons and holes that diffuse on to the surface of the semiconductor interact with water and oxygen molecules by emitting of light. During this interaction, electrons and holes act as acceptors and donors respectively. Holes provide hydroxyl (OH-) radicals by reacting with H_2O and electrons provide superoxide ($O2^{-}\bullet$) radicals by reacting with O_2. Hydrogen ion (H^+) that occurs with the reaction of holes and H_2O produces the hydrogen peroxide. Photocatalytic process of TiO_2 includes chemical steps that produce reactive products

such as hydrogen radicals, hydrogen peroxide and superoxide. These reactive oxides degrade organic molecules and micro organisms [3,4].

4. RESULTS AND CONCLUSION

1. XPS analysis for annealed TiO_2 coated thin film shows that the surface is completely coated by TiO_2 phase. As the number of dips increases, the thickness increases which results the decrease in transparency.
2. Samples coated with TiO_2 thin films have superhydrophilic surfaces at 300 °C. It is observed that TiO_2 thin film on glass after exposing soot dirty show obvious self-cleaning effect under UV light.

In this study, samples coated with TiO_2 thin films by one dip has obvious superhydrophilic property after annealing at 300 °C for 30 minutes. Increasing both the number of dips and annealing temperature causes waste of time as well as in cost.

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