The effect of TiO₂ thin film thickness on self-cleaning glass properties

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Abstract. TiO₂ is one of semiconductor materials which are widely used as photocatalyst in the form of a thin film. The TiO₂ thin film is prepared by using the spin coating sol-gel method. The researcher prepared TiO₂ thin film with 3 coating variations and X-Ray Diffraction characterization, UV-Vis Spectrophotometer, Electron Microscopy Scanning, and examined its hydrophilic and anti-fogging properties. The result of X-Ray Diffraction showed that the phase formed is the anatase on 101 crystal field. The Electron Microscopy Scanning images showed that TiO₂ thin films had a homogeneous surface with the particle sizes as big as 235 nm, 179 nm, and 137 nm. The thickness of each thin film was 2.06 μm, 3.33 μm, and 5.20 μm. The characterization of UV-Vis Spectrophotometer showed that the greatest absorption to the wavelength of visible light was in the thin film’s thickness of 3 coatings with the band-gap determined by using 3.30 eV, 3.33 eV, and 3.33 eV Plot Tuoc. These results indicated that the rate of absorption would be increased by increasing the thickness of film. The increasing thickness of the thin film makes the film hydrophilic able to be used as an anti-fogging substance.

1. Introduction

The use of glass remains to be a choice for buildings in the 21st century [1]. Besides the improved knowledge on the properties of transparent materials, glass also beautifies the property and becomes an alternative to save energy [2] due to its benefits in regard with the room lighting and heating of a building. The development of glass production process leads to a more widespread use of this material in almost all parts of buildings [3]. Glass is a transparent material that also has several shortcomings, such as being contaminated by dirt if it is not cleaned gradually which will cause the reduction of lighting in a room and even can damage the surface of the material. Hence, it is necessary to find a solution to handle such problems. Various strategies have been used to modify these materials in order to assist human’s work, one of which is through the surface engineering technology [4].

In recent years, Titanium dioxide (TiO₂) is the most extensive material to be investigated [5]. Titania thin film morphology plays an important role in capturing sunlight. The existence of different crystalline phases of TiO₂ will affect the effectiveness of photon energy absorption by TiO₂ thin film [6–8]. The photoactive TiO₂ crystalline phases cover the anatase and rutile phases with energy gap (Eg) respectively of 3.2 and 3.0 eV. In addition, the morphology of the TiO₂ thin film surface affects the distinctive adsorption capacity [9,10]. Different morphologies provide different and long adsorption capacities. The amount of organic pollutants adsorbed on the TiO₂ thin layer will affect the
effectiveness of the interaction between h+ species or radical -OH and the persistent organic pollutants [7].

One application of titania film is as photocatalyst [10]. Photo catalysis has been widely applied in life, especially after the discovered hydrophilic nature on the surface of TiO₂ thin films. This application is then constantly evolving as anti-fogging and self-cleaning[11]. One small example of the usefulness of photocatalytic anti-fogging applications is the use of TiO₂ thin films on glass [12].

Chun et al, (2010) synthesized TiO₂ films through the use of sol-gel method by using titanium precursor isopropoxide (TTIP), with a hydrolysis process which was carried out under N₂ atmosphere conditions. The obtained results acquired a percentage of transmittance as big as 90%. According to B.-H. Moon (2013),[13] sol-gel method is commonly used in the synthesis of thin film or modification of pore since its multilayer deposition can control the structure, composition, and activity of the thin film’s result. F. Gherardi (2016) [4] synthesized TiO₂ films by using a TTIP precursor added by HCl and ethyl alcohol and stirred with a magnetic stirrer for 1 hour. After that, the coating on glass substrates was done via spin coating method. The film was calcined at the temperature varied of 250°C, 300°C and 350°C. Transmittance test results showed that the temperature of 350°C by using XRD was already known in the form of crystalline anatase with the transmittance measurement of as big as 90%.

Based on the description of data in the preliminary study and some research done by other researchers, anti-fogging materials made of hydrophilic TiO₂ thin films on a glass substrate, affected by the variations of lap time on the spin coating. However, the effect of coating variations is lack investigated. Therefore, in this study we investigated the effect of the thickness of the TiO₂ thin films grown on glass with coating variations to structural properties, morphology and self-cleaning properties. TiO₂ thin films were synthesized by using sol-gel method. In addition, the hydrophobic properties and anti-fogging of TiO₂ thin films at different thickness will be discussed.

2. Experimental method

The preparation stage is to prepare the used material, which is a glass substrate of 2.5 x 2.5 x 0.1 cm. This substrate preparation included cleaning the substrate prior to be coated by using the material. This is very important as it would determine the bonding film of the substrate. The glass substrate was cleaned / washed in 96% alcohol for 15 minutes and acetone for 15 minutes. The substrate was then dried in an oven at 100°C for 30 minutes. The next stage is the synthesis of TiO₂ sol-gel to produce a solution of TiO₂, 99% TiCl₄ (precursor) and 96% ethanol (solvent) with the ratio of precursor and solvent volume as big as 1: 1. The solution was stirred by using an 800-rpm magnetic stirrer for 60 minutes at room temperature, so the solution was mixed entirely. As the solution had been mixed with salt hydrolysis reaction, the equation was:

\[
\text{TiCl}_4 + 2\text{C}_2\text{H}_5\text{OH} \rightarrow \text{TiO}_2 + 4\text{HCl} + 4\text{CH}_2
\]

(1)

The solution that would be formed was still in the form of sol and it would form a gel after the polyvinyl alcohol solution (PVA) was added. Both solutions were mixed and stirred by using an 800 rpm magnetic stirrer for 60 minutes so that the solution was completely mixed. The process of making the thin film was done by taking four drops of TiO₂ solution to the dripped substrate that has been placed on the spin coating apparatus. Next, the substrate which has been etched with a solution of TiO₂ was rotated at 1500 rpm rotational speed. The next step was preheating, followed by heating (annealing) which was performed by using the furnace at 500°C temperature for 1 hour. The variations in thickness were done in1x, 2x, 3x coating. Annealing process was done in order to improve the structure of the crystal.

The crystalline structure was measured by an X-ray diffractometer (Philips Brand Expert-ProType) in 2θ range from 20° to 80° by 2° s⁻¹ steps. The UV–vis spectroscopy of the films was taken by a spectrophotometer (SP-300) from 320 nm to 800 nm wavelengths. The thickness of the films was measured by the optical interference method. The morphology and thickness of the TiO₂ thin films were characterized by using SEM (Scanning Electron Microscopy-Electron Dispersive Analysis X-
Ray) FEI Brand Inpect-S50 Type. The hydrophilic property of the films was evaluated by measuring the contact angle of distilled water droplet through the use of software Image J.

3. Results and discussions

![Graph showing diffraction patterns of TiO$_2$ thin film at different coating variations](image1)

**Figure 1.** The diffraction pattern of TiO$_2$ thin film at different coating variations

Figure 1 shows the diffraction patterns of TiO$_2$ thin films with different coating variations. The peak was formed on TiO$_2$ films at scattering angle around 25 degrees. This peak was related to TiO$_2$ anatase crystalline structure at crystal planes 101 as observed by Chu et al. (2016). Chu et al. stated that crystals grew with anatase structure at about 550°C[10]. The (101) plane peak then analyzed using Scherrer equation to calculate crystallized grain size as summarized in Table 1.

![Morphology images](image2)

**Figure 2.** Morphology of (a) 1 coating, (b) 2 coatings and, (c) 3 coating of TiO$_2$ Thin Films
Figure 3. Morphology SEM Thickness (a) 1 coating (b) 2 coating and (c) 3 coating of TiO$_2$ Thin Films

The result of SEM can be seen in Figure 2. Based on the existing scale, the average thickness of one coating surface was 0.2 $\mu$m. There were white particles indicating that the impurities did exist during the coating process. The thickness average of the two coating surface was 0.3 $\mu$m, while the thickness average of the three coating surface was 0.5 $\mu$m.

| Thickness TiO$_2$ thin films | 1 coating | 2 coating | 3 coating |
|-----------------------------|-----------|-----------|-----------|
| Crystal grain sizes         | 235 nm    | 179 nm    | 137 nm    |

Table 1. The crystal grain sizes

Table 1 and Figure 3 show that the sample with a crystal grain size was small since it was basically one big crystal with an orientation at producing diffraction peaks approaching the vertical axis. Small-sized crystals that generated peak width as small crystals have a limited X-ray reflectance field. The diffraction peaks generated by constructive interference light was reflected by the crystal fields. The thicker the thin film, the smaller the grain size of crystals formed. The smaller the crystal grain size, the more the cavities formed, so that there would be more surface area to absorb free radicals.

Figure 4 shows the relationship between the $\alpha h$ as a function of $h$ of TiO$_2$ thin film at different coating variations. The value of $\alpha h^n$ obtained from absorbance measurement by using UV-Vis spectrophotometer in the wavelength ranged between 320 nm and 800 nm. The optical band gap calculation was started from the determination of the maximum and minimum transmittance, thick and thin film absorption coefficient and ended by applying the method of Tauc plot calculation. Transmittance measurements performed at the wavelength of 320 nm - 800 nm started with the ultraviolet light to visible light.

$$\alpha h = b(hv - E_g)^n$$

Where $\alpha$ = absorption coefficient, $hv$ = photon energy (eV), $b$ = constants. Value n (n = 2) or (n = 1/2).

Figure 4. The $\alpha h^n$ as function of hv at different coating variations

On this calculation, the largest indirect band gap is about 3.30 eV, 3.33 eV and 3.33 eV as shown in Figure 4.
Figure 5. Contact angle before sun-drenched of (a) 1 coating, (b) 2 coatings, (c) 3 coatings, and after sun-drenched (c') 1 coating, (b') 2 coatings, and (c') 3 coatings

The contact angle measurement was performed by using water droplets. The contact angle between the water and the material was analyzed by using ImageJ software. Small contact angle could be achieved when a stable form hydroxyl grouped on the surface. Hence, when the water appeared, it could be directly bound to these hydroxyl groups. The results obtained from this process are shown in Figure 5. The water contact angle and thin films surface between 20°-40° were still within the range of hydrophilic properties.

Figure 6. Test as anti-fogging Thin Film TiO₂ at a) glass b) TiO₂ film/glass

Figure 6 is the result of anti-fogging test done by spraying water onto the surface of the glass substrate which has successfully grown TiO₂ thin film and the glass substrate which was not coated at all. Hydrophilic nature which was seen on the substrate could grow TiO₂ thin films, direct water spread to form a layer (not formed / droplet of water), whereas the uncoated glass piece was seen on granules / water droplet. Thus, it is evident that the glass thin film which grows TiO₂ has hydrophilic properties, so as to form a hydrophilic layer of water.

4. Conclusion
The TiO₂ thin films are successfully grown on glass substrate via sol-gel method. The crystal structure formed through this process is anatase on a 101 plane. Along with the addition of the thickness of a film, the absorption increases at the same time, and the band gap obtained is approximately 3.33 eV. Conforming to the big band gap, the thin film surface possess a hydrophilic nature so that it could be used as anti-fogging.
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